A NEW WEAK FIELD COUPLING SCHEME FOR COMPLEXES AND APPLICATION OF COMPLETE d^3 ENERGY LEVEL CALCULATIONS TO SOME TETRAGONAL CHROMIUM (III) COMPLEXES

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I dedicate this work to Jesus of Nazareth.

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In the well-known weak field sequence of perturbations, which is called {L,S,J} coupling scheme, one considers the spin-orbit interaction immediately after the interelectronic repulsions but prior to the ligand field potential. For $3d^n$ systems the spin-orbit interaction is not large relative to the ligand field potential. Therefore, it is of value to obtain energy levels in a coupling scheme, {L,S,X}, which considers the ligand field potential prior to the spin-orbit interaction. We have devised this new {L,S,X} sequence, for both cubic and tetragonal symmetry, for the case of d^3 (and d^7) electronic configuration. We have found that the {L,S,X} sequence yields purer eigenfunctions than does the {L,S,J} sequence. We have also compared the {L,S,X} weak field sequence with the well-known strong field sequence. To expand this comparison we have devised an additional tetragonal strong field coupling scheme. We find in the cubic limit, for both d^3 and d^7, that the strong field sequence yields purer eigenfunctions than the comparable weak field sequence. We find in the tetragonal limit that the strong field sequence yields purer eigenfunctions for d^3 but for d^7 in a strong tetragonal field it is the $\{L,S,X\}$ sequence which yields the purest eigenfunctions. In general, we find that considering the spin-orbit interaction as the last perturbation in the sequence yields purer eigenfunctions than would be obtained if the spin-orbit interaction were considered earlier in the sequence. Lastly, we have, using complete energy level calculations, fitted the spectra of some tetragonal chromium (III) complexes in which the five lowest energy intraconfigurational doublets have been identified.

CHAPTER I

INTRODUCTION

Crystal field theory attempts to rationalize the spectral and magnetic properties of transition metal compounds with a simple electrostatic model. In this model the ligands, i.e., the entities directly bound to the central ion, are considered to be point charges or point dipoles fixed in space about the central transition metal ion. The electric field generated by the ligands (henceforth "the ligand field") gives rise to a splitting of the d-orbitals of the metal ion. This splitting of the electronic energy levels of the free ion upon complex formation can be determined qualitatively by symmetry arguments alone, as has been shown by Bethe.[1]

An important application of crystal field theory is in the interpretation of the near infrared, visible and near ultraviolet absorption spectra of coordination compounds. These low intensity bands are now generally recognized as arising due to electronic transitions between the no longer degenerate d-orbitals.

When quantitative calculations of the electronic energy levels are undertaken with the ligands approximated as point charges or point dipoles very poor agreement with experimental data is obtained.[2]

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[1] H. Bethe, Ann. Physik., [5], 3, 807(1935)

[2] S. Sugano, Y. Tanabe and H. Kamimura, Multiplets of Transition-Metal Ions In Crystals, Academic Press, New York, 1970.

This is not surprising since the simple electrostatic theory neglects all covalent bonding and attempts to describe the many electron and, often, the many atom ligands as just point charges or dipoles.

Molecular orbital theory,[1] which takes account of ligand-metal orbital overlap, gives probably the best description of bonding in transition metal compounds. Unfortunately, quantitative molecular orbital calculations have to be carried out for virtually every single system and it is difficult to generalize the results for a series of systems.

The hybrid of the best points of crystal field theory and molecular orbital theory is found in modern ligand field theory.[2] Qualitative aspects of the crystal field theory and the molecular orbital theory can be obtained on the basis of symmetry arguments alone. Ligand field theory incorporates the symmetry aspects of both the theories but rather than attempting to calculate the energy differences rigorously, they are taken as adjustable parameters. These ligand field parameters are then obtained by fitting the absorption spectra of each complex with the calculated parametric energy levels. Ligand field theory is thus the parametric form of crystal field theory or of molecular orbital theory.

The Hamiltonian for a free ion, many-electron system is given below

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[1] J. P. Dahl and C. J. Ballhausen, Advan. Quantum Chem., 4, 170 (1968) and references cited therein.

[2] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

$$H = \frac{-h^2}{8\pi^2 M}\nabla^2 - \frac{h^2}{8\pi^2 m}\sum_i \nabla_i{}^2 - \sum_i \frac{ze^2}{r_i}$$

$$+ \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i \xi(r_i)\vec{\ell}_i\cdot\vec{s}_i \;, \qquad (1)$$

where h is Planck's constant,

M is the mass of the nucleus,

∇^2 is the Laplacian, i.e., $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ for the nucleus,

m is the mass of an electron,

$\nabla_i{}^2$ is the Laplacian for the $i^{\underline{th}}$ electron,

ze is the effective nuclear charge,

$-e$ is the charge of a single electron,

r_i is the distance between the nucleus and the $i^{\underline{th}}$ electron,

r_{ij} is the distance between the $i^{\underline{th}}$ and $j^{\underline{th}}$ electrons and

$\xi(r_i)\vec{\ell}_i\cdot\vec{s}_i$ is the term in the Hamiltonian due to the interaction of the magnetic fields generated by the spin and orbital angular momenta of the electron, this is called the "spin-orbit interaction."

The Hamiltonian for a free ion, many-electron system can be rewritten as

$$H = H^{o} + \sum_{i<j} \frac{e^{2}}{r_{ij}} + \sum_{i} \xi(r_i)\vec{\ell}_i \cdot \vec{s}_i \qquad (2)$$

where H^{o} is a sum of one electron and free ion Hamiltonians and the terms which arise due to the interelectronic repulsions and the spin-orbit interaction are considered to be perturbations.

When a free ion forms a complex, a fourth term is added to the Hamiltonian: the ligand field potential (V_{LF}). This potential is due to the coulombic repulsions between the central ion's d electron and the ligands. The ligand field potential has the form

$$V_{LF}(x_i) = \sum_{k} \frac{q_k e}{r_{ik}} \quad , \qquad (3)$$

where x_i is the coordinate of the $i^{\underline{th}}$ electron,

$-q_k$ is the magnitude of the charge on the $k^{\underline{th}}$ ligand, and

r_{ik} is the distance between the $i^{\underline{th}}$ electron and the $k^{\underline{th}}$ ligand.

There are now three perturbations to be added on to the single electron Hamiltonian: the interelectronic repulsions, the spin-orbit interaction, and the ligand field potential.

The order in which the perturbations are considered will follow the decreasing order of the magnitude credited to each effect. This is reflected in the secular determinant in the extent to which each perturbation is diagonalized.

In the strong field approach we consider the ligand field potential first. In (j,j) coupling we carry out the spin-orbit interaction as the first perturbation. Lastly, in the weak field procedure we consider the interelectronic repulsions to be the first perturbation.

For transition metal complexes, especially for first row transition metal complexes, the spin-orbit interaction is always a minor perturbation relative to the interelectronic repulsions and the ligand field potential.[1] Therefore, the (j,j) coupling approach, which implies that the spin-orbit interaction is the major perturbation, is inappropriate for transition metal complexes (especially first row transition metal complexes). For this reason, we will be concerned only with the weak field and the strong field approaches.

After specifying which perturbation will be taken first, we must still decide the order of the remaining perturbations. Clearly, there are two possibilities for each of the three approaches we have just described. Each particular sequence of perturbations is known as a coupling scheme or a representation.

When complete configuration interaction is included all coupling schemes for a given electronic configuration and symmetry will yield the same set of eigenvalues. However, how apt the description of the eigenfunctions is, in terms of the basis eigenvectors of the coupling scheme, will be dependent on the sequence of perturbations chosen. Thus, the choice of an appropriate coupling scheme is important because only then can reasonable parentages be ascribed to the various levels and a reasonable approximation to the true eigenfunction be gained from the basis eigenvectors. Also, if configuration interaction is neglected, the various coupling schemes for a given electronic configuration and symmetry will no longer yield identical sets of eigenvalues. With neglect of configuration interaction only an appropriate coupling scheme (i.e., a coupling scheme in which the sequence of perturbations reflects the relative magnitudes of the perturbations) will yield a reasonable approximation to the true set of eigenvalues.

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[1] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

Thus, for the octahedral (O_h) case there are two possible weak field and two possible strong field coupling schemes. These coupling schemes can be represented as shown in Table 1. Henceforth, we will refer to the octahedral case as the cubic case.

To date only the $\{L,S,J\}$ sequence of perturbations has been used in complete weak field calculations.[1] The $\{L,S,J\}$ sequence

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[1] A. D. Liehr, J. Phys. Chem., 64, 43(1960), (d^1 and d^9); A. D. Liehr and C. J. Ballhausen, Ann. Phys., (N.Y.), 6, 134(1959), (d^2 and d^8); H. A. Weakliem, J. Chem. Phys., 36, 2117(1962), (d^3 and d^7); J. P. Jesson, J. Chem. Phys., 48, 161(1968), (d^3 and d^7); J. Ferguson, Aust. J. Chem., 23, 635(1970), (d^3 and d^7); T. M. Dunn and Wai-Kee Li, J. Chem. Phys., 47, 3783(1967); Erratum, Ibid., 53, 2132(1970), (d^4 and d^6); E. Konig and S. Kremer, Z. Naturforschung, 29a , 31(1974), (d^4 and d^6); Wai-Kee Li, Spectrochim. Acta, 24A, 1573(1968); Erratum, Ibid., 2289(1971), (d^5); E. Konig, R. Schnakig and S. Kremer, Z. Naturforschung, 29a, 419(1974), (d^5); W. Low and G. Rosengasten, J. Mol. Spec., 12, 319(1964), (d^5).

TABLE 1

Weak and Strong Field Coupling Schemes
in Cubic Symmetry

Sequence of Perturbations	Title of the Coupling Scheme
e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_{LF}	$\{L,S,J\}$
e^2/r_{ij}, then V_{LF}, then $\xi(r)\vec{\ell}\cdot\vec{s}$	$\{L,S,X\}$
V_{LF}, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then e^2/r_{ij}	$\{x^C,\gamma^C,\Gamma^C\}$
V_{LF}, then e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$	$\{x^C,X^C,\Gamma^C\}$

has been found convenient because it follows the free ion sequence of perturbations. That is, when carrying out an $\{L,S,J\}$ coupling scheme one need not repeat the calculations for the first two perturbations (the interelectronic repulsions and the spin-orbit interaction). This duplication of the free ion case for the first two perturbations greatly reduces the computational effort required in an $\{L,S,J\}$ coupling scheme relative to the other cubic coupling schemes.

As we have mentioned, for complexes of the 3d transition metals, in particular for those members with low atomic numbers, the spin-orbit interaction's effect is small and can often be neglected. Therefore, obtaining energy levels in the $\{L,S,X\}$ weak field coupling scheme, in which the spin-orbit interaction can be considered to be a minor perturbation relative to the ligand field potential, could be of value.

The first and the main purpose of this investigation is to devise the new $\{L,S,X\}$ coupling scheme for the various d^n electronic configurations and to demonstrate the superiority of the $\{L,S,X\}$ coupling scheme over the $\{L,S,J\}$ coupling scheme for the first row transtion metal ions.

We have previously carried out the $\{L,S,X\}$ coupling scheme for the case of d^2 (and d^8) electronic configuration.[1] Here we extend the $\{L,S,X\}$ coupling scheme to the case of d^3 (and d^7) electronic configuration.

The $\{x^C,\gamma^C,\Gamma^C\}$ cubic strong field coupling scheme considers the spin-orbit interaction as the second perturbation. Hence, the $\{x^C,\gamma^C,\Gamma^C\}$ coupling scheme is the strong field analog to the $\{L,S,J\}$ weak field coupling scheme. The $\{x^C,X^C,\Gamma^C\}$ cubic strong field coupling scheme considers the spin-orbit interaction as the last perturbation. It is likely that the $\{x^C,X^C,\Gamma^C\}$ scheme, in which the spin-orbit interaction is the last perturbation considered, is more appropriate for first row transition metal complexes than is the

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[1] J. A. Collins and J. R. Perumareddi, Theoret. Chim. Acta, 54, 325 (1980).

$\{x^C,\gamma^C,\Gamma^C\}$ scheme, in which the spin-orbit interaction is the second perturbation considered. The $\{x^C,X^C,\Gamma^C\}$ cubic strong field coupling scheme for the case of d^3 (and d^7) electronic configuration has been carried out by Eisenstein.[1] We have repeated the calculation of the $\{x^C,X^C,\Gamma^C\}$ scheme for the case of d^3 (and d^7) electronic configuration in order to have available to us the requisite wave functions so as to be able to extend this strong field coupling scheme to a lower symmetry.

When the symmetry of the complex is lowered from O_h to D_{4h}, either by substitution or by distortion, then the ligand field changes from cubic to tetragonal. We denote the ligand field potential of tetragonal (or quadrate) symmetry by V_Q. It is also possible to express the tetragonal potential as a sum of cubic (V_C) and axial (V_a) potentials,[2] as is illustrated in Fig. 1. In this latter case, tetragonal energy levels are obtained by going through the cubic levels and finding how they are perturbed by the axial field potential.

We have seen that two weak field schemes are feasible for cubic symmetry: the {L,S,J} and the {L,S,X} coupling schemes. The {L,S,J} sequence of perturbations gives rise to two coupling schemes in tetragonal symmetry. In the first coupling scheme the cubic and the axial fields can be considered separately, always taking the cubic field first since the added axial field acts as a small perturbation

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[1] J. C. Eisenstein, J. Chem. Phys., 34, 1628(1961).

[2] J. R. Perumareddi, Phys. Stat. Sol. (b), 59, K127(1973).

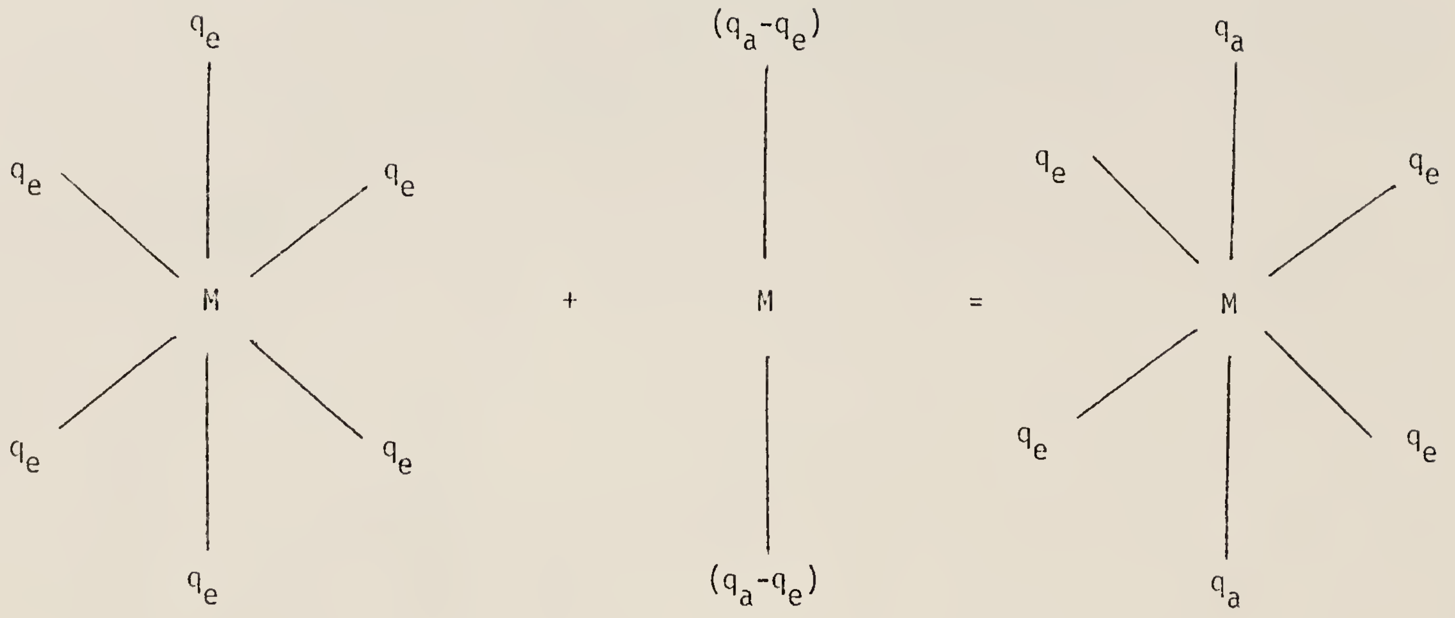

Figure 1. The Tetragonal Ligand Field Potential as a Sum of Cubic and Axial Fields.

to the cubic field, both after spin-orbit interaction. In the second coupling scheme the cubic and the axial fields may be taken together, after the spin-orbit interaction.

The $\{L,S,X\}$ sequence of perturbations gives rise to three coupling schemes in tetragonal symmetry. When the cubic and the axial fields are taken separately, the axial field may be considered either before or after the spin-orbit interaction. The third scheme results when the tetragonal potential is applied as a whole before the spin-orbit interaction.

The two cubic and the five tetragonal weak field coupling schemes are listed in Table 2 with special emphasis being placed on the cubic parentage of the tetragonal coupling schemes.

We have carried out the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ and the $\{L,S,X^C,X^Q,\Gamma^Q\}$ tetragonal weak field coupling schemes for d^3 (and d^7) electronic configuration. The $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ tetragonal scheme is an extension of the $\{L,S,X\}$ cubic scheme. The $\{L,S,X^Q,\Gamma^Q\}$ tetragonal weak field coupling scheme differs only slightly from the $\{L,S,X^C,X^Q,\Gamma^Q\}$ tetragonal weak field scheme.[1] Therefore, we have not carried out the $\{L,S,X^Q,\Gamma^Q\}$ scheme for the case of d^3 (and d^7) electronic configuration.

The d^3 wave functions and the Hamiltonian (energy) matrices for the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ and the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling schemes will be presented along with the details of their derivation.

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[1] J. A. Collins, Master's Thesis, Florida Atlantic University, 1976.

TABLE 2

Weak Field Coupling Schemes for Cubic and Tetragonal Symmetries

Sequence in Cubic	Sequence in Tetragonal	Title of the Tetragonal Coupling Schemes
e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_c	e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_c, then V_a	$\{L,S,J,\Gamma^C,\Gamma^Q\}$
	e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_Q	$\{L,S,J,\Gamma^Q\}$
e^2/r_{ij}, then V_c, then $\xi(r)\vec{\ell}\cdot\vec{s}$	e^2/r_{ij}, then V_c, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_a	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$
	e^2/r_{ij}, then V_c, then V_a, then $\xi(r)\vec{\ell}\cdot\vec{s}$	$\{L,S,X^C,X^Q,\Gamma^Q\}$
	e^2/r_{ij}, then V_Q, then $\xi(r)\vec{\ell}\cdot\vec{s}$	$\{L,S,X^Q,\Gamma^Q\}$

The strong field approach yields six coupling schemes when the symmetry is lowered from cubic to tetragonal. The two cubic and the six tetragonal strong field coupling schemes are listed in Table 3. A special emphasis has been placed, in Table 3, on the cubic parentage of the tetragonal coupling schemes.

The $\{x^C,\gamma^C,\Gamma^C,\Gamma^Q\}$ and $\{x^C,\gamma^C,\gamma^Q,\Gamma^Q\}$ strong field coupling schemes consider the spin-orbit interaction as the second perturbation, prior to the interelectronic repulsions. The $\{x^Q,\gamma^Q,\Gamma^Q\}$ strong field coupling scheme also considers the spin-orbit interaction prior to the interelectronic repulsions. It is unlikely, especially for complexes of first row transition metal ions, that the spin-orbit interaction would be more important than the interelectronic repulsions. Consequently, the $\{x^C,\gamma^C,\Gamma^C,\Gamma^Q\}$, $\{x^C,\gamma^C,\gamma^Q,\Gamma^Q\}$ and $\{x^Q,\gamma^Q,\Gamma^Q\}$ strong field schemes are not expected to be important for complexes of the transition metal ions (especially those of the first row).

The $\{x^Q,X^Q,\Gamma^Q\}$ strong field coupling scheme considers the interelectronic repulsions prior to the spin-orbit interaction but after the axial ligand field perturbation. This sequence of perturbations is almost certainly an improvement over those of the three previously mentioned strong field coupling schemes in which the spin-orbit interaction is taken prior to the interelectronic repulsions. Nonetheless, the axial ligand field is often due to a relatively small distortion in the cubic environment and, as such, is not expected to be of greater importance than the interelectronic repulsions. The $\{x^Q,X^Q,\Gamma^Q\}$ scheme might well find application in the study of

TABLE 3

Strong Field Coupling Schemes for Cubic and Tetragonal Symmetries

Sequence in Cubic	Sequence in Tetragonal	Title of the Tetragonal Coupling Schemes
V_c, then e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$	V_c, then e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_a	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
	V_c, then e^2/r_{ij}, then V_a, then $\xi(r)\vec{\ell}\cdot\vec{s}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$
	V_Q, then e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$	$\{x^Q,X^Q,\Gamma^Q\}$
V_c, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then e^2r_{ij}	V_c, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then e^2/r_{ij}, then V_a	$\{x^C,\gamma^C,\Gamma^C,\Gamma^Q\}$
	V_c, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_a, then e^2/r_{ij}	$\{x^C,\gamma^C,\gamma^Q,\Gamma^Q\}$
	V_Q, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then e^2/r_{ij}	$\{x^Q,\gamma^Q,\Gamma^Q\}$

square planar complexes. A square planar complex is, of course, an extreme case of tetragonal distortion in which two transligands are completely removed.

The $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ strong field coupling schemes both consider the interelectronic repulsions as the second perturbation. It is likely that of the six possible strong field schemes the $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ schemes are the most appropriate for trans-disubstituted and moderately distorted octahedral complexes.

The $\{x^C,X^C,X^Q,\Gamma^Q\}$ coupling scheme has been carried out recently by Perumareddi for d^3 (and d^7) electronic configuration.[1]

As the second purpose of this investigation we have carried out the $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ strong field coupling scheme for d^3 (and d^7) electronic configuration, in order to compare this tetragonal coupling scheme with the $\{x^C,X^C,X^Q,\Gamma^Q\}$ strong field coupling scheme and with the two tetragonal weak field coupling schemes which we have carried out. The $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ tetragonal scheme is an extension of the $\{x^C,X^C,\Gamma^C\}$ cubic scheme.

The d^3 wave functions and the Hamiltonian (energy) matrices for the $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme will be presented along with the details of their derivation.

The detailed comparison of the various coupling schemes for d^3 (and d^7) electronic configuration and both cubic and tetragonal symmetries will be presented. This comparison will be based on the percent purities of the eigenfunctions yielded by each scheme.

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[1] J. R. Perumareddi, to be published.

The spin-orbit interaction usually need not be included in the interpretation of the spin-allowed d-d spectra of transition metal complexes. This is so because the spin-orbital components of the spin-allowed bands are seldom resolved. The interpretation of the spin-forbidden transitions, however, requires the inclusion of the spin-orbit interaction. As the third purpose of this investigation we will attempt the fitting of the spectra of some tetragonal chromium (III) complexes, taken from the literature. The complexes that we have chosen are those in the spectra of which all the expected low energy intraconfigurational spin-forbidden doublets have been identified.

CHAPTER II

THE WEAK FIELD COUPLING SCHEMES

The Interelectronic Repulsions--Free Ion Terms[1]

In the weak field coupling schemes the interelectronic repulsions constitute the first perturbation. Hence, we need calculate only once the interelectronic repulsion energies for all of the weak field schemes. Furthermore, the wave functions derived in order to calculate the free ion interelectronic repulsion energies will serve as the basis functions for the other perturbations in the weak field coupling schemes.

The three electron wave functions are normalized Slater determinants;[2] that is for ψ_1,ψ_2,ψ_3 wave functions for three isolated electrons, with total generalized coordinates X_1,X_2,X_3 respectively, we define the three-electron wave function (Ψ) by

$$\Psi(X_1,X_2,X_3) = \begin{vmatrix} \psi_1(X_1) & \psi_1(X_2) & \psi_1(X_3) \\ \psi_2(X_1) & \psi_2(X_2) & \psi_2(X_3) \\ \psi_3(X_1) & \psi_3(X_2) & \psi_3(X_3) \end{vmatrix} / \sqrt{3} \qquad (4)$$

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[1] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, University Press, Cambridge, 1951.

[2] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

$$= (\psi_1(X_1)\psi_2(X_2)\psi_3(X_3) - \psi_1(X_1)\psi_2(X_3)\psi_3(X_2)$$

$$- \psi_1(X_2)\psi_2(X_1)\psi_3(X_3) + \psi_1(X_2)\psi_2(X_3)\psi_3(X_1)$$

$$+ \psi_1(X_3)\psi_2(X_1)\psi_3(X_2) - \psi_1(X_3)\psi_2(X_2)\psi_3(X_1))/\sqrt{6} .$$

These wave functions are anti-symmetric in accordance with the Pauli exclusion principle. Throughout, we will use a shorthand notation in which the fact that the wave functions are Slater determinants will be understood. Thus, we will write the above expansion of $\Psi(X_1,X_2,X_3)$ as simply $(\psi_1(1)\psi_2(2)\psi_3(3))$ or even more briefly as $(\psi_1\psi_2\psi_3)$.

For a 3d electron the four principal quantum numbers are

$$n = 3 \tag{5a}$$

$$\ell = 2 \tag{5b}$$

$$m_\ell = \pm 2,\ \pm 1,\ 0 \tag{5c}$$

and

$$m_s = \pm 1/2 \ . \tag{5d}$$

As usual, we have assumed the single electron hydrogen-like orbitals for the many electron case.

For the many electron case we have the quantum numbers L, S, M_L and M_S, where

$$M_L = \sum(m_{\ell_i}) \qquad \text{and} \tag{6a}$$

$$M_S = \sum(m_{s_i}) \tag{6b}$$

with the summation being over all the electrons. The L and S are analogous to the single electron quantum numbers ℓ and s. Thus, we have

$$M_L = L, L-1, \ldots, -L \quad \text{and} \tag{7a}$$

$$M_S = S, S-1, \ldots, -S \; . \tag{7b}$$

The Pauli principle states that no two electrons can have the same wave function. Therefore, 3d electrons in the same system must differ in either m_ℓ or m_s. Furthermore, due to interelectronic repulsions, not all the L and S combinations allowed by the Pauli principle will have the same energy. For each electronic configuration, we need to pick out the allowed combinations of L and S, known as "terms," and, in order to calculate the energies, determine the wave functions associated with each term.

We shall use the Russell-Saunders (L-S coupling) procedure[1] for finding the energies corresponding to the terms. This is a parametric method the details of which we will now describe for the case of d^3 outer electronic configuration.

For a $3d^3$ ion we can construct the microstate table as shown in Table 4, obeying at all times the Pauli principle.

In writing the microstates the fact that $n=3$ and $\ell=2$ is understood. Thus, the microstate $(2\bar{2}1)$ means that electron one has

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[1] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

TABLE 4

The Weak Field Microstate Table for d^3

M_S M_L	+3/2	+1/2	-1/2	-3/2
+5		$(2\bar{2}1)$	$(2\bar{2}\bar{1})$	
+4		$(2\bar{2}0)$ $(21\bar{1})$	$(2\bar{2}\bar{0})$ $(\bar{2}1\bar{1})$	
+3	(210)	$(21\bar{0})$ $(2\bar{1}0)$ $(\bar{2}10)$ $(2\bar{2}-1)$	$(\bar{2}\bar{1}0)$ $(\bar{2}1\bar{0})$ $(2\bar{1}\bar{0})$ $(2\bar{2}-\bar{1})$	$(\bar{2}\bar{1}\bar{0})$
+2	$(21-1)$	$(21-\bar{1})$ $(2\bar{1}-1)$ $(\bar{2}1-1)$ $(2\bar{2}-2)$ $(20\bar{0})$ $(1\bar{1}0)$	$(\bar{2}\bar{1}-1)$ $(\bar{2}1-\bar{1})$ $(2\bar{1}-\bar{1})$ $(2\bar{2}-\bar{2})$ $(\bar{2}0\bar{0})$ $(1\bar{1}\bar{0})$	$(\bar{2}\bar{1}-\bar{1})$
+1	$(21-2)$ $(20-1)$	$(21-\bar{2})$ $(2\bar{1}-2)$ $(\bar{2}1-2)$ $(20-\bar{1})$ $(2\bar{0}-1)$ $(\bar{2}0-1)$ $(10\bar{0})$ $(1\bar{1}-1)$	$(\bar{2}\bar{1}-2)$ $(\bar{2}1-\bar{2})$ $(2\bar{1}-\bar{2})$ $(\bar{2}\bar{0}-1)$ $(\bar{2}0-\bar{1})$ $(2\bar{0}-\bar{1})$ $(\bar{1}0\bar{0})$ $(1\bar{1}-\bar{1})$	$(\bar{2}\bar{1}-\bar{2})$ $(\bar{2}\bar{0}-\bar{1})$
0	$(20-2)$ $(10-1)$	$(20-\bar{2})$ $(2\bar{0}-2)$ $(\bar{2}0-2)$ $(\bar{1}0-1)$ $(1\bar{0}-1)$ $(10-\bar{1})$ $(1\bar{1}-2)$ $(2-1-\bar{1})$	$(\bar{2}\bar{0}-2)$ $(\bar{2}0-\bar{2})$ $(2\bar{0}-\bar{2})$ $(\bar{1}\bar{0}-1)$ $(\bar{1}0-\bar{1})$ $(1\bar{0}-\bar{1})$ $(1\bar{1}-\bar{2})$ $(\bar{2}-1-\bar{1})$	$(\bar{2}\bar{0}-\bar{2})$ $(\bar{1}\bar{0}-\bar{1})$

The rest are obvious

m_ℓ equal to +2 and m_s equal to +1/2, that electron two has m_ℓ equal to +2 and m_s equal to -1/2, and that electron three has m_ℓ equal to +1 and m_s equal to +1/2. Obviously, the microstate (221) or $(\bar{2}\bar{2}1)$ is not possible.

We can now derive the Russell-Saunders terms (L-S coupling terms) which we denote by

$$(2S+1)_L \quad , \tag{8}$$

where symbols are used for L as shown in Table 5.

TABLE 5

Term Symbols

L	Symbol
0	S
1	P
2	D
3	F
4	G
5	H
6	I

The spin multiplicity is given by (2S+1) and the orbital multiplicity by (2L+1). Thus, the total multiplicity of a term is given by the product (2S+1)(2L+1).

The microstate $(2\bar{2}1)$ yields $M_L = 5$ which, being the maximum M_L possible, belongs to a term of $L=5$. Since for this term M_S

can only be +1/2 or -1/2, then S is 1/2. Therefore, we have a ^2H term whose total multiplicty is 22. The $^2H(22)$ term requires a microstate in each box from $M_L = +5$ to $M_L = -5$ with $M_S = +1/2$ and -1/2, 22 in all.

Turning to the microstate $(2\bar{2}0)$ we have $M_L = 4$. Now $M_L = 4$ is maximum since the microstate $(2\bar{2}1)$ has already been claimed by ^2H. Thus, $(2\bar{2}0)$ belongs to a term with $L = 4$. Since for this term M_S can be only +1/2 or -1/2 then, $S = 1/2$. Therefore, we have a ^2G term whose total multiplicity is 18. The $^2G(18)$ term requires a microstate in each box from $M_L = 4$ to $M_L = -4$ with $M_S = +1/2$ and -1/2, 18 in all.

The microstate (210) has $M_L = 3$, now the maximum possible, and $M_S = 3/2$, also the maximum. Therefore, we have a ^4F term whose total multiplicty is 28. The $^4F(28)$ term requires a microstate in each box from $M_L = 3$ to $M_L = -3$ with $M_S = 3/2$, 1/2, -1/2, and -3/2, 28 in all.

Continuing we find a $^2F(14)$ term, two $^2D(10)$ terms, a $^4P(12)$ term and a $^2P(6)$ term.

In summary, for d^3 we have the following terms: $^2H(22)$, $^2G(18)$, $^4F(28)$, $^2F(14)$, $^2D\text{-}a(10)$, $^2D\text{-}b(10)$, $^4P(12)$ and $^2P(6)$.

Now we must decide which microstates or linear combinations of microstates are eigenfunctions of the $\hat{L}$ and $\hat{S}$ terms (the circumflex indicates an operator). The appropriate combinations of the microstates will then serve as the wave functions for the terms and will be known as the $|L,S;M_L,M_S>$ functions.

When only one microstate has a particular M_L and M_S combination, this is straightforward. Thus, since only the microstate $(2\bar{2}1)$ has $M_L = 5$ and $M_S = 1/2$, the function $|5,1/2;5,1/2>$ is $(2\bar{2}1)$ and is one of the 22 eigenfunctions of ^2H. There are two microstates with $M_L = 4$ and $M_S = 1/2$; these are $(2\bar{2}0)$ and $(21\bar{1})$. Finding the linear combination of these two microstates that is the eigenfunction $|5,1/2;4,1/2>$ of ^2H is our problem. Application of the angular momentum raising and lowering operators,[1] $\hat{L}_\pm$ and $\hat{S}_\pm$, will allow us to form the proper $|L,S;M_L,M_S>$ functions for ^2H. The use of these raising and lowering operators is illustrated below.

$$\hat{L}_+|L,M_L> = \hbar[(L+M_L+1)(L-M_L)]^{1/2}|L,M_L+1> \tag{9a}$$

$$\hat{L}_-|L,M_L> = \hbar\ (L-M_L+1)(L+M_L)]^{1/2}|L,M_L-1> \tag{9b}$$

$$\hat{S}_+|S,M_S> = \hbar[(S+M_S+1)(S-M_S)]^{1/2}|S,M_S+1> \tag{9c}$$

$$\hat{S}_-|S,M_S> = \hbar[(S-M_S+1)(S+M_S)]^{1/2}|S,M_S-1> \tag{9d}$$

The operators are to be applied to each electron separately; that is,

$$\hat{L}_\pm = \hat{\ell}_\pm(1) + \hat{\ell}_\pm(2) + \ldots\hat{\ell}_\pm(n) \tag{10a}$$

and

$$\hat{S}_\pm = \hat{s}_\pm(1) + \hat{s}_\pm(2) + \ldots\hat{s}_\pm(n) \tag{10b}$$

when there are n electrons.

---

[1] C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill Book Co., New York, 1962.

Thus,

$$L_-|5,1/2;5,1/2\rangle = \hbar[(5-5+1)(5+5)]^{1/2}|5,1/2;4,1/2\rangle$$

$$= [\hat{\ell}_-(1) + \hat{\ell}_-(2) + \hat{\ell}_-(3)](2\bar{2}1)$$

$$= \hbar[(2-2+1)(2+2)]^{1/2}(1\bar{2}1) + \hbar[(2-2+1)(2+2)]^{1/2}(2\bar{1}1)$$

$$+ \hbar[(2-1+1)(2+1)]^{1/2}(2\bar{2}0)$$

so

$$|5,1/2;4,1/2\rangle = [\sqrt{3}(2\bar{2}0) - \sqrt{2}(21\bar{1})]/\sqrt{5}.$$

By repeated application of these operators we can derive the complete set of $|L,S;M_L,M_S\rangle$ functions for the ^2H term.

For the ^2G term we do not have a unique microstate for any M_L and M_S combination to begin the analysis with. For the box corresponding to $M_L = 4$ and $M_S = 1/2$ we have the linear combination of $(2\bar{2}0)$ and $(21\bar{1})$ which is the function $|5,1/2;4,1/2\rangle$ of ^2H. We know that the function $|4,1/2;4,1/2\rangle$ of ^2G must be orthogonal to $|5,1/2;4,1/2\rangle$ of ^2H. Also, we have the normalization condition. Using these two conditions we can write down $|4,1/2;4,1/2\rangle$ of ^2G. This function is

$$|4,1/2;4,1/2\rangle = [\sqrt{2}(2\bar{2}0) + \sqrt{3}(21\bar{1})]/\sqrt{5} \quad .$$

Note that the choice of phase for $|4,1/2;4,1/2\rangle$ of ^2G is initially arbitrary but once made must be adhered to throughout. Then by application of the appropriate raising and lowering operators we can derive the complete set of $|L,S;M_L,M_S>$ functions for the ^2G term.

For ^4F we have a unique microstate with $M_L = 3$ and $M_S = 3/2$. Thus, the function $|3,3/2;3,3/2>$ is (210). Applying $\hat{S}_-$ we obtain

$$\hat{S}_-|3,3/2;3,3/2> = \hbar[(3/2-3/2+1)(3/2+3/2)]^{1/2}|3,3/2;3,1/2>$$

$$= [\hat{S}_-(1) + \hat{S}_-(2) + \hat{S}_-(3)](210)$$

$$= \hbar[(1/2-1/2+1)(1/2+1/2)]^{1/2}(\bar{2}10)$$

$$+ \hbar[(1/2-1/2+1)(1/2+1/2)]^{1/2}(2\bar{1}0) + \hbar[(1/2-1/2+1)(1/2+1/2)]^{1/2}(21\bar{0})$$

and

$$|3,3/2;3,1/2) = [(\bar{2}10) + (2\bar{1}0) + (21\bar{0})]/\sqrt{3} \quad .$$

Continued application of the appropriate raising and lowering operators allows us to derive the complete set of $|L,S;M_L,M_S>$ functions for the ^4F term.

The use of orthonormality and the raising and lowering operators allow us to determine the $|L,S;M_L,M_S>$ functions for the other terms (^2F, ^2D-a, ^2D-b, ^4P and ^2P) as well. The case of the two ^2D terms (^2D-a and ^2D-b) is particularly difficult since two independent functions must be found simultaneously for the same M_L and M_S combinations.[1]

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[1] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, University Press, Cambridge, 1951.

The complete set of the $|L,S;M_L,M_S>$ functions for the d^3 terms is given in Table 6.

In the perturbation theory of degenerate systems one constructs a secular determinant which is then diagonalized to obtain the perturbation energies. In the case of the interelectronic repulsion perturbation the microstates are the unperturbed basis functions and what Russell-Saunders coupling does is to obtain the $|L,S;M_L,M_S>$ eigenfunctions as the linear combinations of these basis functions that diagonalize the perturbation matrix. Also, for a term of definite L and S the set of (2S+1)(2L+1) states will have the same energy since the energy is independent of M_S and M_L.

The energy of a term then is calculated by the expression

$$E' = \int \Psi^* H' \Psi d\tau \tag{11}$$

where Ψ is the $|L,S;M_L,M_S>$ function of that term and H' is the interelectronic repulsion perturbation $(\sum_{i<j} e^2/r_{ij})$. For ^2D a 2 by 2 secular determinant is formed.

We can expand $1/r_{ij}$ in terms of the well-known spherical harmonics,[1] $Y_\ell^{m_\ell}(\theta,\phi)$:

$$\frac{1}{r_{ij}} = \sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{+\ell} \frac{4\pi}{(2\ell+1)} \cdot \frac{r_<^\ell}{r_>^{\ell+1}} \cdot Y_\ell^{m_\ell^*}(\theta_i,\phi_i) \cdot Y_\ell^{m_\ell}(\theta_j,\phi_j) \tag{12}$$

where $r_<$ is the lesser and $r_>$ the greater of the two distances r_i and r_j and $Y_\ell^{m_\ell}(\theta,\phi)$ are the spherical harmonics.

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[1] H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry, John Wiley and Sons, Inc., New York, 1944.

TABLE 6

The $|L,S;M_L,M_S>$ Functions for d^3

---

^2P

$$
\begin{aligned}
|1,1/2;1,1/2> = {} & (-4\sqrt{3}(21\text{-}\bar{2})+2\sqrt{3}(2\bar{1}\text{-}2)+2\sqrt{3}(\bar{2}1\text{-}2)+4\sqrt{2}(20\text{-}\bar{1})+\sqrt{2}(2\bar{0}\text{-}1) \\
& -5\sqrt{2}(\bar{2}0\text{-}1)-3\sqrt{3}(1\bar{1}\text{-}1)-3\sqrt{3}(10\bar{0}))/\sqrt{210}
\end{aligned}
$$

$$
\begin{aligned}
|1,1/2;0,1/2> = {} & (-4(20\text{-}\bar{2})-3\sqrt{6}(1\bar{1}\text{-}2)+8(2\bar{0}\text{-}2)-4(\bar{2}0\text{-}2)-(10\text{-}\bar{1})+3\sqrt{6}(2\text{-}1\text{-}\bar{1}) \\
& +2(1\bar{0}\text{-}1)-(\bar{1}0\text{-}1))/\sqrt{210}
\end{aligned}
$$

$$
\begin{aligned}
|1,1/2;-1,1/2>= {} & (2\sqrt{3}(2\text{-}1\text{-}\bar{2})-5\sqrt{2}(10\text{-}\bar{2})+4\sqrt{2}(1\bar{0}\text{-}2)+\sqrt{2}(\bar{1}0\text{-}2)+2\sqrt{3}(2\text{-}\bar{1}\text{-}2) \\
& -4\sqrt{3}(\bar{2}\text{-}1\text{-}2)+3\sqrt{3}(1\text{-}1\text{-}\bar{1})+3\sqrt{3}(0\bar{0}\text{-}1))/\sqrt{210}
\end{aligned}
$$

$$
\begin{aligned}
|1,1/2;1,-1/2>= {} & (-2\sqrt{3}(\bar{2}1\text{-}\bar{2})-2\sqrt{3}(2\bar{1}\text{-}\bar{2})+4\sqrt{3}(\bar{2}\bar{1}\text{-}2)+5\sqrt{2}(2\bar{0}\text{-}\bar{1})-4\sqrt{2}(\bar{2}\bar{0}\text{-}1) \\
& -\sqrt{2}(\bar{2}0\text{-}\bar{1})-3\sqrt{3}(1\bar{1}\text{-}\bar{1})-3\sqrt{3}(\bar{1}0\bar{0}))/\sqrt{210}
\end{aligned}
$$

$$
\begin{aligned}
|1,1/2;0,-1/2>= {} & (-8(\bar{2}0\text{-}\bar{2})-3\sqrt{6}(1\bar{1}\text{-}\bar{2})+4(\bar{2}\bar{0}\text{-}2)+4(2\bar{0}\text{-}\bar{2})-2(\bar{1}0\text{-}\bar{1}) \\
& +3\sqrt{6}(\bar{2}\text{-}1\text{-}\bar{1})+(\bar{1}\bar{0}\text{-}1)+(1\bar{0}\text{-}\bar{1}))/\sqrt{210}
\end{aligned}
$$

$$
\begin{aligned}
|1,1/2;-1-1/2>= {} & (5\sqrt{2}(\bar{1}\bar{0}\text{-}2)-\sqrt{2}(\bar{1}0\text{-}\bar{2})-4\sqrt{2}(1\bar{0}\text{-}\bar{2})+4\sqrt{3}(2\text{-}\bar{1}\text{-}\bar{2})-2\sqrt{3}(\bar{2}\text{-}\bar{1}\text{-}2) \\
& -2\sqrt{3}(\bar{2}\text{-}1\text{-}\bar{2})+3\sqrt{3}(\bar{1}\text{-}1\text{-}\bar{1})+3\sqrt{3}(0\bar{0}\text{-}\bar{1}))/\sqrt{210}
\end{aligned}
$$

$^2D\text{-}a$

$$|2,1/2;2,1/2> = ((2\bar{1}\text{-}1)+(20\bar{0})-(2\bar{2}\text{-}2)-(21\text{-}\bar{1}))/2$$

$$|2,1/2;1,1/2> = ((1\bar{1}\text{-}1)+(10\bar{0})+(\bar{2}1\text{-}2)-(21\text{-}\bar{2}))/2$$

$$|2,1/2;0,1/2> = ((10\text{-}\bar{1})+(\bar{2}0\text{-}2)-(\bar{1}0\text{-}1)-(20\text{-}\bar{2}))/2$$

$$|2,1/2;-1,1/2>= ((1\text{-}1\text{-}\bar{1})+(\bar{2}\text{-}1\text{-}2)+(0\bar{0}\text{-}1)-(2\text{-}1\text{-}\bar{2}))/2$$

TABLE 6--Continued

$|2,1/2;-2,1/2> \;=\; ((\bar{1}-1-2)+(0\bar{0}-2)-(2-2-\bar{2})-(1-\bar{1}-2))/2$

$|2,1/2;2,-1/2> \;=\; ((\bar{2}\bar{1}-1)+(\bar{2}0\bar{0})-(2\bar{2}-\bar{2})-(\bar{2}1-\bar{1}))/2$

$|2,1/2;1,-1/2> \;=\; ((1\bar{1}-\bar{1})+(\bar{1}0\bar{0})+(\bar{2}\bar{1}-2)-(2\bar{1}-\bar{2}))/2$

$|2,1/2;0,-1/2> \;=\; ((1\bar{0}-\bar{1})+(\bar{2}\bar{0}-2)-(\bar{1}\bar{0}-1)-(2\bar{0}-\bar{2}))/2$

$|2,1/2;-1,-1/2> \;=\; ((\bar{1}-1-\bar{1})+(\bar{2}-\bar{1}-2)+(0\bar{0}-\bar{1})-(2-\bar{1}-\bar{2}))/2$

$|2,1/2;-2,-1/2> \;=\; ((\bar{1}-1-\bar{2})+(0\bar{0}-\bar{2})-(\bar{2}-2-\bar{2})-(1-\bar{1}-\bar{2}))/2$

---

^{2}D-b

$|2,1/2;2,1/2> \;=\; (3(21-\bar{1})-5(2\bar{2}-2)+(2\bar{1}-1)-4(\bar{2}1-1)-3(20\bar{0})$
$-2\sqrt{6}(1\bar{1}0))/\sqrt{84}$

$|2,1/2;1,1/2> \;=\; (3(21-\bar{2})+(\bar{2}1-2)-4(2\bar{1}-2)-(1\bar{1}-1)+3(10\bar{0})$
$-2\sqrt{6}(\bar{2}0-1)+2\sqrt{6}(2\bar{0}-1))\sqrt{84}$

$|2,1/2;0,1/2> \;=\; (3(20-\bar{2})-2\sqrt{6}(1\bar{1}-2)-3(\bar{2}0-2)-3(\bar{1}0-1)$
$+3(10-\bar{1})-2\sqrt{6}(2-1-\bar{1}))/\sqrt{84}$

$|2,1/2;-1,1/2> \;=\; (2\sqrt{6}(10-\bar{2})-(2-1-\bar{2})-2\sqrt{6}(1\bar{0}-2)-3(\bar{2}-1-2)$
$+3(0\bar{0}-1)-(1-1-\bar{1})+4(2-\bar{1}-2))/\sqrt{84}$

$|2,1/2;-2,1/2> \;=\; (4(1-1-\bar{2})-5(2-2-\bar{2})-3(0\bar{0}-2)-(1-\bar{1}-2)$
$-3(\bar{1}-1-2)-2\sqrt{6}(0-1-\bar{1}))/\sqrt{84}$

$|2,1/2;2,-1/2> \;=\; (4(2\bar{1}-\bar{1})-5(2\bar{2}-\bar{2})-3(\bar{2}\bar{1}-1)-(\bar{2}1-\bar{1})$
$-3(\bar{2}0\bar{0})-2\sqrt{6}(1\bar{1}\bar{0}))/\sqrt{84}$

TABLE 6--Continued

$$\begin{aligned}|2,1/2;1,-1/2> &= (4(\bar{2}1-\bar{2})-3(\bar{2}\bar{1}-2)-(2\bar{1}-\bar{2})-(1\bar{1}-\bar{1})+3(\bar{1}0\bar{0})\\ &\quad -2\sqrt{6}(\bar{2}0-\bar{1})+2\sqrt{6}(2\bar{0}-\bar{1}))/\sqrt{84}\end{aligned}$$

$$\begin{aligned}|2,1/2;0,-1/2> &= (3(2\bar{0}-\bar{2})-2\sqrt{6}(1\bar{1}-\bar{2})-3(\bar{2}\bar{0}-2)-3(\bar{1}\bar{0}-1)\\ &\quad +3(1\bar{0}-\bar{1})-2\sqrt{6}(\bar{2}-1-\bar{1}))/\sqrt{84}\end{aligned}$$

$$\begin{aligned}|2,1/2;-1,-1/2> &= (2\sqrt{6}(\bar{1}0-\bar{2})-2\sqrt{6}(\bar{1}\bar{0}-2)-4(\bar{2}-1-\bar{2})+3(0\bar{0}-\bar{1})\\ &\quad -(\bar{1}-1-\bar{1})+(\bar{2}-\bar{1}-2)+3(2-\bar{1}-\bar{2}))/\sqrt{84}\end{aligned}$$

$$\begin{aligned}|2,1/2;-2-1/2> &= ((\bar{1}-1-\bar{2})+3(1-\bar{1}-\bar{2})-5(\bar{2}-2-\bar{2})-3(0\bar{0}-\bar{2})\\ &\quad -4(\bar{1}-\bar{1}-2)-2\sqrt{6}(\bar{0}-1-\bar{1}))/\sqrt{84}\end{aligned}$$

${}^{2}F$

$$|3,1/2;3,1/2> = (\sqrt{6}(2\bar{2}-1)+2(\bar{2}10)-(21\bar{0})-(2\bar{1}0))/2\sqrt{3}$$

$$|3,1/2;2,1/2> = ((2\bar{1}-1)+2(2\bar{2}-2)-\sqrt{6}(1\bar{1}0)-(21-\bar{1}))/2\sqrt{3}$$

$$\begin{aligned}|3,1/2;1,1/2> &= (-2\sqrt{2}(1\bar{1}-1)+\sqrt{3}(2\bar{0}-1)+3\sqrt{2}(2\bar{1}-2)-2\sqrt{2}(\bar{2}1-2)\\ &\quad +3\sqrt{2}(10\bar{0})-\sqrt{3}(20-\bar{1})-\sqrt{2}(21-\bar{2}))/\sqrt{60}\end{aligned}$$

$$\begin{aligned}|3,1/2;0,1/2> &= (2(\bar{1}0-1)-4(1\bar{0}-1)+\sqrt{6}(1\bar{1}-2)-\sqrt{6}(2-1-\bar{1})+4(2\bar{0}-2)\\ &\quad -2(\bar{2}0-2)+2(10-\bar{1})-2(20-\bar{2}))/\sqrt{60}\end{aligned}$$

$$\begin{aligned}|3,1/2;-1,1/2> &= (2\sqrt{2}(1-1-\bar{1})-3\sqrt{2}(0\bar{0}-1)-\sqrt{3}(\bar{1}0-2)+\sqrt{3}(1\bar{0}-2)\\ &\quad +3\sqrt{2}(2-\bar{1}-2)-2\sqrt{2}(2-1-\bar{2})-\sqrt{2}(\bar{2}-1-2))/\sqrt{60}\end{aligned}$$

$$|3,1/2;-2,1/2> = (\sqrt{6}(0-1-\bar{1})+(1-\bar{1}-2)-2(2-2-\bar{2})-(\bar{1}-1-2))/2\sqrt{3}$$

$$|3,1/2;-3,1/2> = (2(0-1-\bar{2})-(0-\bar{1}-2)-\sqrt{6}(1-2-\bar{2})-(\bar{0}-1-2))/2\sqrt{3}$$

TABLE 6--Continued

$|3,1/2;3,-1/2> \;=\; (\sqrt{6}(2\bar{2}-\bar{1})+(\bar{2}\bar{1}0)+(\bar{2}1\bar{0})-2(2\bar{1}\bar{0}))/2\sqrt{3}$

$|3,1/2;2,-1/2> \;=\; ((\bar{2}\bar{1}-1)+2(2\bar{2}-\bar{2})-\sqrt{6}(1\bar{1}\bar{0})-(\bar{2}1-\bar{1}))/2\sqrt{3}$

$|3,1/2;1,-1/2> \;=\; (-2\sqrt{2}(1\bar{1}-\bar{1})+\sqrt{3}(\bar{2}\bar{0}-1)+\sqrt{2}(\bar{2}\bar{1}-2)+2\sqrt{2}(2\bar{1}-\bar{2})$
$-3\sqrt{2}(\bar{2}1-\bar{2})+3\sqrt{2}(\bar{1}0\bar{0})-\sqrt{3}(\bar{2}0-\bar{1}))/\sqrt{60}$

$|3,1/2;0,-1/2> \;=\; (4(\bar{1}0-\bar{1})-2(\bar{1}\bar{0}-1)-2(1\bar{0}-\bar{1})+\sqrt{6}(1\bar{1}-\bar{2})-\sqrt{6}(\bar{2}-1-\bar{1})$
$+2(\bar{2}\bar{0}-2)+2(2\bar{0}-\bar{2})-4(\bar{2}0-\bar{2}))/\sqrt{60}$

$|3,1/2;-1,-1/2> \;=\; (2\sqrt{2}(\bar{1}-1-\bar{1})-3\sqrt{2}(0\bar{0}-\bar{1})-\sqrt{3}(\bar{1}0-\bar{2})+\sqrt{3}(1\bar{0}-\bar{2})$
$+2\sqrt{2}(\bar{2}-\bar{1}-2)+\sqrt{2}(2-\bar{1}-\bar{2})-3\sqrt{2}(\bar{2}-1-\bar{2}))/\sqrt{60}$

$|3,1/2;-2,-1/2> \;=\; (\sqrt{6}(\bar{0}-1-\bar{1})+(1-\bar{1}-\bar{2})-2(\bar{2}-2-\bar{2})-(\bar{1}-1-\bar{2}))/2\sqrt{3}$

$|3,1/2;-3,-1/2> \;=\; ((\bar{0}-1-\bar{2})+(0-\bar{1}-\bar{2})-2(\bar{0}-\bar{1}-2)-\sqrt{6}(\bar{1}-2-\bar{2}))/2\sqrt{3}$

---

^2G

$|4,1/2;4,1/2> \;=\; (\sqrt{2}(2\bar{2}0)+\sqrt{3}(21\bar{1}))/\sqrt{5}$

$|4,1/2;3,1/2> \;=\; (3(21\bar{0})-2(\bar{2}10)-(2\bar{1}0)+\sqrt{6}(2\bar{2}-1))/2\sqrt{5}$

$|4,1/2;2,1/2> \;=\; (4\sqrt{3}(20\bar{0})+3\sqrt{3}(21-\bar{1})+\sqrt{2}(1\bar{1}0)+4\sqrt{3}(\bar{2}1-1)$
$+\sqrt{3}(2\bar{1}-1)+2\sqrt{3}(2\bar{2}-2))/2\sqrt{35}$

$|4,1/2;1,1/2> \;=\; (\sqrt{6}(10\bar{0})-3(2\bar{0}-1)+7(20-\bar{1})+\sqrt{6}(21-\bar{2})+2\sqrt{6}(1\bar{1}-1)$
$-4(\bar{2}0-1)-2\sqrt{6}(\bar{2}1-2)+\sqrt{6}(2\bar{1}-2))/2\sqrt{35}$

$|4,1/2;0,1/2> \;=\; (\sqrt{2}(10-\bar{1})+\sqrt{3}(2-1-\bar{1})+\sqrt{2}(20-\bar{2})-\sqrt{2}(\bar{1}0-1)$
$+\sqrt{3}(1\bar{1}-2)-\sqrt{2}(\bar{2}0-2))/\sqrt{14}$

TABLE 6--Continued

$$\begin{aligned}|4,1/2;-1,1/2\rangle &= (2\sqrt{6}(1-1-\bar{1})+4(10-\bar{2})-\sqrt{6}(2-\bar{1}-2)+2\sqrt{6}(2-1-\bar{2})\\ &\quad+\sqrt{6}(0\bar{0}-1)-7(\bar{1}0-2)+3(1\bar{0}-2)-\sqrt{6}(\bar{2}-1-2))/2\sqrt{35}\end{aligned}$$

$$\begin{aligned}|4,1/2;-2,1/2\rangle &= (\sqrt{2}(0-1-\bar{1})-\sqrt{3}(1-\bar{1}-2)+4\sqrt{3}(1-1-\bar{2})+2\sqrt{3}(2-2-\bar{2})\\ &\quad+4\sqrt{3}(0\bar{0}-2)-3\sqrt{3}(\bar{1}-1-2))/2\sqrt{35}\end{aligned}$$

$$|4,1/2;-3,1/2\rangle = ((0-\bar{1}-2)+2(0-1-\bar{2})+\sqrt{6}(1-2-\bar{2})-3(\bar{0}-1-2))/2\sqrt{5}$$

$$|4,1/2;-4,1/2\rangle = (\sqrt{3}(-1-\bar{1}-2)+\sqrt{2}(0-2-\bar{2}))/\sqrt{5}$$

$$|4,1/2;4,-1/2\rangle = (\sqrt{2}(2\bar{2}\bar{0})+\sqrt{3}(\bar{2}1\bar{1}))/\sqrt{5}$$

$$|4,1/2;3,-1/2\rangle = ((\bar{2}1\bar{0})+2(2\bar{1}\bar{0})-3(\bar{2}\bar{1}0)+\sqrt{6}(2\bar{2}-\bar{1}))/2\sqrt{5}$$

$$\begin{aligned}|4,1/2;2,-1/2\rangle &= (4\sqrt{3}(\bar{2}0\bar{0})+4\sqrt{3}(2\bar{1}-\bar{1})+\sqrt{2}(1\bar{1}\bar{0})-3\sqrt{3}(\bar{2}\bar{1}-1)\\ &\quad-\sqrt{3}(\bar{2}1-\bar{1})+2\sqrt{3}(2\bar{2}-\bar{2}))/2\sqrt{35}\end{aligned}$$

$$\begin{aligned}|4,1/2;1,-1/2\rangle &= (\sqrt{6}(\bar{1}0\bar{0})-7(\bar{2}\bar{0}-1)+3(\bar{2}0-\bar{1})+4(2\bar{0}-\bar{1})+2\sqrt{6}(2\bar{1}-\bar{2})\\ &\quad+2\sqrt{6}(1\bar{1}-\bar{1})-\sqrt{6}(\bar{2}\bar{1}-2)-\sqrt{6}(\bar{2}1-\bar{2}))/2\sqrt{35}\end{aligned}$$

$$\begin{aligned}|4,1/2;0,-1/2\rangle &= (\sqrt{2}(1\bar{0}-\bar{1})+\sqrt{3}(\bar{2}-1-\bar{1})+\sqrt{2}(2\bar{0}-\bar{2})-\sqrt{2}(\bar{1}\bar{0}-1)\\ &\quad+\sqrt{3}(1\bar{1}-\bar{2})-\sqrt{2}(\bar{2}\bar{0}-2))/\sqrt{14}\end{aligned}$$

$$\begin{aligned}|4,1/2;-1,-1/2\rangle &= (2\sqrt{6}(\bar{1}-1-\bar{1})+7(1\bar{0}-\bar{2})-2\sqrt{6}(\bar{2}-\bar{1}-2)+\sqrt{6}(\bar{2}-1-\bar{2})\\ &\quad+\sqrt{6}(2-\bar{1}-\bar{2})+\sqrt{6}(0\bar{0}-\bar{1})-4(\bar{1}\bar{0}-2)-3(\bar{1}0-\bar{2}))/2\sqrt{35}\end{aligned}$$

$$\begin{aligned}|4,1/2;-2-1/2\rangle &= (\sqrt{2}(\bar{0}-1-\bar{1})+\sqrt{3}(\bar{1}-1-\bar{2})+3\sqrt{3}(1-\bar{1}-\bar{2})+2\sqrt{3}(\bar{2}-2-\bar{2})\\ &\quad+4\sqrt{3}(0\bar{0}-\bar{2})-4\sqrt{3}(\bar{1}-\bar{1}-2))/2\sqrt{35}\end{aligned}$$

TABLE 6--Continued

$|4,1/2;-3,-1/2\rangle = (3(0-\bar{1}-\bar{2})+\sqrt{6}(\bar{1}-2-\bar{2})-2(\bar{0}-\bar{1}-2)-(\bar{0}-1-\bar{2}))/2\sqrt{5}$

$|4,1/2;-4,-1/2\rangle = (\sqrt{3}(-1-\bar{1}-\bar{2})+\sqrt{2}(\bar{0}-2-\bar{2}))/\sqrt{5}$

---

^{2}H

$|5,1/2;5,1/2\rangle = (2\bar{2}1)$

$|5,1/2;4,1/2\rangle = (\sqrt{3}(2\bar{2}0)-\sqrt{2}(21\bar{1}))/\sqrt{5}$

$|5,1/2;3,1/2\rangle = (\sqrt{3}(2\bar{2}-1)-\sqrt{2}(21\bar{0})+\sqrt{8}(2\bar{1}0)-\sqrt{2}(\bar{2}10))/\sqrt{15}$

$|5,1/2;2,1/2\rangle = (\sqrt{6}(1\bar{1}0)-3(20\bar{0})-(21-\bar{1})+3(2\bar{1}-1)-2(\bar{2}1-1)+(2\bar{2}-2))/\sqrt{30}$

$|5,1/2;1,1/2\rangle = (8(1\bar{1}-1)-6(10\bar{0})+3\sqrt{6}(2\bar{0}-1)-2\sqrt{6}(20-\bar{1})-(21-\bar{2})$
$+4(2\bar{1}-2)-\sqrt{6}(\bar{2}0-1)-3(\bar{2}1-2))/\sqrt{210}$

$|5,1/2;0,1/2\rangle = (4(1\bar{0}-1)-2(\bar{1}0-1)+\sqrt{6}(1\bar{1}-2)-\sqrt{6}(2-1-\bar{1})-(20-\bar{2})$
$+2(2\bar{0}-2)-(\bar{2}0-2)-2(10-\bar{1}))/\sqrt{42}$

$|5,1/2;-1,1/2\rangle = (6(0\bar{0}-1)-8(1-1-\bar{1})+3\sqrt{6}(1\bar{0}-2)-2\sqrt{6}(\bar{1}0-2)$
$+4(2-\bar{1}-2)-3(2-1-\bar{2})-\sqrt{6}(10-\bar{2})-(\bar{2}-1-2))/\sqrt{210}$

$|5,1/2;-2,1/2\rangle = (-\sqrt{6}(0-1-\bar{1})+3(0\bar{0}-2)-2(1-1-\bar{2})+3(1-\bar{1}-2)$
$-(\bar{1}-1-2)-(2-2-\bar{2}))/\sqrt{30}$

$|5,1/2;-3,1/2\rangle = (\sqrt{8}(0-\bar{1}-2)-\sqrt{2}(0-1-\bar{2})-\sqrt{2}(\bar{0}-1-2)-\sqrt{3}(1-2-\bar{2}))/\sqrt{15}$

$|5,1/2;-4,1/2\rangle = (-\sqrt{3}(0-2-\bar{2})+\sqrt{2}(-1-\bar{1}-2))/\sqrt{15}$

$|5,1/2;-5,1/2\rangle = -(-1-2-\bar{2})$

TABLE 6--Continued

$|5,1/2;5,-1/2> = (2\bar{2}\bar{1})$

$|5,1/2;4,-1/2> = (\sqrt{3}(2\bar{2}\bar{0})-\sqrt{2}(\bar{2}1\bar{1}))/\sqrt{5}$

$|5,1/2;,3,-1/2> = (\sqrt{3}(2\bar{2}-\bar{1})-\sqrt{8}(\bar{2}1\bar{0})+\sqrt{2}(\bar{2}\bar{1}0)+\sqrt{2}(2\bar{1}\bar{0}))/\sqrt{15}$

$|5,1/2;2,-1/2> = (\sqrt{6}(1\bar{1}\bar{0})-3(\bar{2}0\bar{0})-3(\bar{2}1-\bar{1})+(\bar{2}\bar{1}-1)$
$+2(2\bar{1}-\bar{1})+(2\bar{2}-\bar{2}))/\sqrt{30}$

$|5,1/2;1,-1/2> = (8(1\bar{1}-\bar{1})-6(\bar{1}0\bar{0})+2\sqrt{6}(\bar{2}\bar{0}-1)+\sqrt{6}(2\bar{0}-\bar{1})-3\sqrt{6}(\bar{2}0-\bar{1})$
$-4(\bar{2}1-\bar{2})+(\bar{2}\bar{1}-2)+3(2\bar{1}-\bar{2}))/\sqrt{210}$

$|5,1/2;0,-1/2> = (2(\bar{1}\bar{0}-1)+2(1\bar{0}-\bar{1})-4(\bar{1}0-\bar{1})+\sqrt{6}(1\bar{1}-\bar{2})-\sqrt{6}(\bar{2}-1-\bar{1})$
$-2(\bar{2}0-\bar{2})+(\bar{2}\bar{0}-2)+(2\bar{0}-\bar{2}))/\sqrt{42}$

$|5,1/2;-1,-1/2> = (6(0\bar{0}-\bar{1})-8(\bar{1}-1-\bar{1})+\sqrt{6}(\bar{1}\bar{0}-2)+2\sqrt{6}(1\bar{0}-\bar{2})-3\sqrt{6}(\bar{1}0-\bar{2})$
$+3(\bar{2}-\bar{1}-2)+(2-\bar{1}-\bar{2})-4(\bar{2}-1-\bar{2}))/\sqrt{210}$

$|5,1/2;-2,-1/2> = (-\sqrt{6}(\bar{0}-1-\bar{1})+3(0\bar{0}-\bar{2})-3(\bar{1}-1-\bar{2})+2(\bar{1}-\bar{1}-2)$
$+(1-\bar{1}-\bar{2})-(\bar{2}-2-\bar{2}))/\sqrt{30}$

$|5,1/2;-3,-1/2> = (\sqrt{2}(\bar{0}-\bar{1}-2)+\sqrt{2}(0-\bar{1}-\bar{2})-\sqrt{8}(\bar{0}-1-\bar{2})-\sqrt{3}(\bar{1}-2-\bar{2}))/\sqrt{15}$

$|5,1/2;-4,-1/2> = (-\sqrt{3}(\bar{0}-2-\bar{2})+\sqrt{2}(-1-\bar{1}-\bar{2}))/\sqrt{5}$

$|5,1/2;-5,-1/2> = -(-\bar{1}-2-\bar{2})$

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^4P

$|1,3/2;1,3/2> = (\sqrt{2}(20-1)-\sqrt{3}(21-2))/\sqrt{5}$

$|1,3/2;0,3/2> = (2(10-1)-(20-2))/\sqrt{5}$

TABLE 6--Continued

$$|1,3/2;-1,3/2\rangle = (\sqrt{2}(10\text{-}2)-\sqrt{3}(2\text{-}1\text{-}2))/\sqrt{5}$$

$$\begin{aligned}|1,3/2;1,1/2\rangle = {} & (\sqrt{2}(\bar{2}0\text{-}1)+\sqrt{2}(2\bar{0}\text{-}1)+\sqrt{2}(20\text{-}\bar{1})-\sqrt{3}(\bar{2}1\text{-}2)\\ & -\sqrt{3}(2\bar{1}\text{-}2)-\sqrt{3}(21\text{-}\bar{2}))/\sqrt{15}\end{aligned}$$

$$\begin{aligned}|1,3/2;0,1/2\rangle = {} & (2(\bar{1}0\text{-}1)+2(1\bar{0}\text{-}1)+2(10\text{-}\bar{1})-(\bar{2}0\text{-}2)\\ & -(2\bar{0}\text{-}2)-(20\text{-}\bar{2}))/\sqrt{15}\end{aligned}$$

$$\begin{aligned}|1,3/2;-1,1/2\rangle = {} & (\sqrt{2}(\bar{1}0\text{-}2)+\sqrt{2}(1\bar{0}\text{-}2)+\sqrt{2}(10\text{-}\bar{2})-\sqrt{3}(\bar{2}\text{-}1\text{-}2)\\ & -\sqrt{3}(2\text{-}\bar{1}\text{-}2)-\sqrt{3}(2\text{-}1\text{-}\bar{2}))/\sqrt{15}\end{aligned}$$

$$\begin{aligned}|1,3/2;1,-1/2\rangle = {} & (\sqrt{2}(\bar{2}\bar{0}\text{-}1)+\sqrt{2}(\bar{2}0\text{-}\bar{1})+\sqrt{2}(2\bar{0}\text{-}\bar{1})-\sqrt{3}(\bar{2}\bar{1}\text{-}2)\\ & -\sqrt{3}(\bar{2}1\text{-}\bar{2})-\sqrt{3}(2\bar{1}\text{-}\bar{2}))/\sqrt{15}\end{aligned}$$

$$\begin{aligned}|1,3/2;0,-1/2\rangle = {} & (2(\bar{1}\bar{0}\text{-}1)+2(\bar{1}0\text{-}\bar{1})+2(1\bar{0}\text{-}\bar{1})-(\bar{2}\bar{0}\text{-}2)\\ & -(\bar{2}0\text{-}\bar{2})-(2\bar{0}\text{-}\bar{2}))/\sqrt{15}\end{aligned}$$

$$\begin{aligned}|1,3/2;-1,-1/2\rangle = {} & (\sqrt{2}(\bar{1}\bar{0}\text{-}2)+\sqrt{2}(1\bar{0}\text{-}\bar{2})+\sqrt{2}(\bar{1}0\text{-}\bar{2})-\sqrt{3}(\bar{2}\text{-}\bar{1}\text{-}2)\\ & -\sqrt{3}(\bar{2}\text{-}1\text{-}\bar{2})-\sqrt{3}(2\text{-}\bar{1}\text{-}\bar{2}))/\sqrt{15}\end{aligned}$$

$$|1,3/2;1,-3/2\rangle = (\sqrt{2}(\bar{2}\bar{0}\text{-}\bar{1})-\sqrt{3}(\bar{2}\bar{1}\text{-}\bar{2}))/\sqrt{5}$$

$$|1,3/2;0,-3/2\rangle = (2(\bar{1}\bar{0}\text{-}\bar{1})-(\bar{2}\bar{0}\text{-}\bar{2}))/\sqrt{5}$$

$$|1,3/2;-1,-3/2\rangle = (\sqrt{2}(\bar{1}\bar{0}\text{-}\bar{2})-\sqrt{3}(\bar{2}\text{-}\bar{1}\text{-}\bar{2}))/\sqrt{5}$$

^4F

$$|3,3/2;3,3/2\rangle = (210)$$

$$|3,3/2;2,3/2\rangle = (21\text{-}1)$$

TABLE 6--Continued

$|3,3/2;1,3/2\rangle = (\sqrt{3}(20-1)+\sqrt{2}(21-2))/\sqrt{5}$

$|3,3/2;0,3/2\rangle = ((10-1)+2(20-2))/\sqrt{5}$

$|3,3/2;-1,3/2\rangle = (\sqrt{3}(10-2)+\sqrt{2}(2-1-2))/\sqrt{5}$

$|3,3/2;-2,3/2\rangle = (1-1-2)$

$|3,3/2;-3,3/2\rangle = (0-1-2)$

$|3,3/2;3,1/2\rangle = ((\bar{2}10)+(2\bar{1}0)+(21\bar{0}))/\sqrt{3}$

$|3,3/2;2,1/2\rangle = ((\bar{2}1-1)+(2\bar{1}-1)+(21-\bar{1}))/\sqrt{3}$

$|3,3/2;1,1/2\rangle = (\sqrt{3}(\bar{2}0-1)+\sqrt{3}(2\bar{0}-1)+\sqrt{3}(20-\bar{1})+\sqrt{2}(\bar{2}1-2)$
$+\sqrt{2}(2\bar{1}-2)+\sqrt{2}(21-\bar{2}))/\sqrt{15}$

$|3,3/2;0,1/2\rangle = ((\bar{1}0-1)+(1\bar{0}-1)+(10-\bar{1})+2(\bar{2}0-2)$
$+2(2\bar{0}-1)+2(20-\bar{2}))/\sqrt{15}$

$|3,3/2;-1,1/2\rangle = (\sqrt{3}(\bar{1}0-2)+\sqrt{3}(1\bar{0}-2)+\sqrt{3}(10-\bar{2})+\sqrt{2}(\bar{2}-1-2)$
$+\sqrt{2}(2-\bar{1}-2)+\sqrt{2}(2-1-\bar{2}))/\sqrt{15}$

$|3,3/2;-2,1/2\rangle = ((\bar{1}-1-2)+(1-\bar{1}-2)+(1-1-\bar{2}))/\sqrt{3}$

$|3,3/2;-3,1/2\rangle = ((\bar{0}-1-2)+(0-\bar{1}-2)+(0-1-\bar{2}))/\sqrt{3}$

$|3,3/2;3,-1/2\rangle = ((\bar{2}\bar{1}0)+(\bar{2}1\bar{0})+(2\bar{1}\bar{0}))/\sqrt{3}$

$|3,3/2;2,-1/2\rangle = ((\bar{2}\bar{1}-1)+(\bar{2}1-\bar{1})+(2\bar{1}-\bar{1}))/\sqrt{3}$

TABLE 6--Continued

$$\begin{aligned}|3,3/2;1,-1/2\rangle &= (\sqrt{3}(\bar{2}\bar{0}-1)+\sqrt{3}(\bar{2}0-\bar{1})+\sqrt{3}(2\bar{0}-\bar{1})+\sqrt{2}(\bar{2}\bar{1}-2)\\ &\quad +\sqrt{2}(\bar{2}1-\bar{2})+\sqrt{2}(2\bar{1}-\bar{2}))/\sqrt{15}\end{aligned}$$

$$\begin{aligned}|3,3/2;0,-1/2\rangle &= ((\bar{1}\bar{0}-1)+(\bar{1}0-\bar{1})+(1\bar{0}-\bar{1})+2(\bar{2}\bar{0}-2)+(\bar{2}0-\bar{2})\\ &\quad +(2\bar{0}-\bar{2}))/\sqrt{15}\end{aligned}$$

$$\begin{aligned}|3,3/2;-1,-1/2\rangle &= (\sqrt{3}(\bar{1}\bar{0}-2)+\sqrt{3}(\bar{1}0-\bar{2})+\sqrt{3}(1\bar{0}-\bar{2})+\sqrt{2}(\bar{2}-\bar{1}-2)\\ &\quad +\sqrt{2}(\bar{2}-1-\bar{2})+\sqrt{2}(2-\bar{1}-\bar{2}))/\sqrt{15}\end{aligned}$$

$$|3,3/2;-2,-1/2\rangle = ((\bar{1}-\bar{1}-2)+(\bar{1}-1-\bar{2})+(1-\bar{1}-\bar{2}))/\sqrt{3}$$

$$|3,3/2;-3,-1/2\rangle = ((\bar{0}-\bar{1}-2)+(\bar{0}-1-\bar{2})+(0-\bar{1}-\bar{2}))/\sqrt{3}$$

$$|3,3/2;3,-3/2\rangle = (\bar{2}\bar{1}\bar{0})$$

$$|3,3/2;2,-3/2\rangle = (\bar{2}\bar{1}-\bar{1})$$

$$|3,3/2;1,-3/2\rangle = (\sqrt{3}(\bar{2}\bar{0}-\bar{1})+\sqrt{2}(\bar{2}\bar{1}-\bar{2}))/\sqrt{5}$$

$$|3,3/2;0,-3/2\rangle = ((\bar{1}\bar{0}-\bar{1})+2(\bar{2}\bar{0}-\bar{2}))/\sqrt{5}$$

$$|3,3/2;-1,-3/2\rangle = (\sqrt{3}(\bar{1}\bar{0}-\bar{2})+\sqrt{2}(\bar{2}-\bar{1}-\bar{2}))/\sqrt{5}$$

$$|3,3/2;-2,-3/2\rangle = (\bar{1}-\bar{1}-\bar{2})$$

$$|3,3/2;-3,-3/2\rangle = (\bar{0}-\bar{1}-\bar{2})$$

The wave functions associated with the microstates are the single electron wave functions that are the solutions of Schrodinger's equation for the hydrogen atom case. These have the form

$$\psi^{o} = R_{n,\ell}(r)\psi_{\ell}^{m_{\ell}}(\theta,\phi) \tag{13}$$

with $R_{n,\ell}(r)$ being the radially dependent factor. For a 3d ion we will write $R_{n,\ell}(r)$ as $R_{3d}(r)$.

As an example let us consider the calculation of the energy of the ^2H term. We could use any of the 22 degenerate $|L,S;M_L,M_S>$ functions which belong to ^2H. For the sake of simplicity we choose $|5,1/2;5,1/2> = (2\bar{2}1)$. We must use the expanded Slater determinant for the calculation. Thus,

$$|5,1/2;5,1/2> = [(2\bar{2}1)-(21\bar{2})-(\bar{2}21)$$
$$+ (12\bar{2})+(\bar{2}12)-(1\bar{2}2)]/\sqrt{6}\ .$$

The energy of ^2H is given by

$$E'(^2H) = \int_1 \int_2 \int_3 [(2\bar{2}1)-(21\bar{2})-(\bar{2}21)+(12\bar{2})$$
$$+ (\bar{2}12)-(1\bar{2}2)]^{*}(e^2/r_{12} + e^2/r_{13} + e^2/r_{23})[(2\bar{2}1)$$
$$- (21\bar{2})-(\bar{2}21)+(12\bar{2})+(\bar{2}12)-(1\bar{2}2)]d\tau_1\ d\tau_2\ d\tau_3/6 \tag{14}$$

To illustrate the method of calculation let us take a fragment of the above expression for the energy of ^2H. Let us consider only

$$\int_1\int_2\int_3 (2\bar{2}1)^*(e^2/r_{12} + e^2/r_{13} + e^2/r_{23})(2\bar{2}1)d\tau_1\, d\tau_2\, d\tau_3 \quad .$$

Expanding we have

$$\int_1 \alpha(1)^*\alpha(1)ds_1 \int_2 \beta(2)^*\beta(2)ds_2 \int_3 \alpha(3)^*\alpha(3)ds_3 \cdot$$

$$\int_1\int_2\int_3 R_{3d}^*(1)R_{3d}^*(2)R_{3d}^*(3)e^2\Big[\sum_{\ell=0}^{\infty}\frac{r_<^{\ell}}{r_>^{\ell+1}}\Big]R_{3d}(1)R_{3d}(2) \cdot$$

$$R_{3d}(3)r_1^2dr_1r_2^2dr_2r_3^2dr_3 \int_1\int_2\int_3 Y_2^{2^*}(1)Y_2^{2^*}(2) \cdot$$

$$Y_2^{1^*}(3)\Big[\sum_{i<j}^{j=3}\sum_{\ell=0}^{\infty}\sum_{m_\ell=-\ell}^{+\ell} \cdot \frac{4\pi}{(2\ell+1)} \cdot Y_\ell^{m_\ell^*}(\theta_i,\phi_i)Y_\ell^{m_\ell}(\theta_j,\phi_j)\Big] \cdot$$

$$Y_2^2(1)Y_2^2(2)Y_2^1(3)\sin\theta_1 d\theta_1 d\phi_1 \sin\theta_2 d\theta_2 d\phi_2 \sin\theta_3 d\theta_3 d\phi_3 \ .$$

The spin functions are orthornormal, that is

$$\int \alpha^*\alpha ds = \int \beta^*\beta ds = 1 \qquad (15a)$$

and

$$\int \beta^*\alpha ds = \int \alpha^*\beta ds = 0 \qquad (15b)$$

Continuing, we have

$$\int_0^\infty\int_0^\infty\int_0^\infty R_{3d}^*(1)R_{3d}(1)R_{3d}^*(2)R_{3d}(2)R_{3d}^*(3)R_{3d}(3) \cdot$$

$$e^2\Big[\sum_{\ell=0}^{\infty}\frac{r_<^{\ell}}{r_>^{\ell+1}} \cdot\Big]r_1^2dr_1r_2^2dr_2r_3^2dr_3 \cdot$$

$$\int_1 \int_2 \int_3 [Y_2^{2^*}(1)Y_2^{2}(1)Y_2^{2^*}(2)Y_2^{2}(2)Y_2^{1^*}(3)Y_2^{1}(3)] \cdot$$

$$\sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{-\ell} \cdot \frac{4\pi}{(2\ell+1)} [Y_\ell^{m_\ell^*}(\theta_1,\phi_1)\cdot Y_\ell^{m_\ell}(\theta_2,\phi_2) +$$

$$Y_\ell^{m_\ell^*}(\theta_1,\phi_1)Y_\ell^{m_\ell}(\theta_3,\phi_3) + Y_\ell^{m_\ell^*}(\theta_2,\phi_2)Y_\ell^{m_\ell}(\theta_3,\phi_3)] \cdot$$

$$\sin\theta_1 d\theta_1 d\phi_1 \sin\theta_2 d\theta_2 d\phi_2 \sin\theta_3 d\theta_3 d\phi_3 \ .$$

Further,

$$\int_1^{\infty} \int_2^{\infty} \int_3^{\infty} [R_{3d}^{*}(1)R_{3d}(1)R_{3d}^{*}(2)R_{3d}(2)R_{3d}^{*}(3)R_{3d}(3)]\cdot$$

$$e^2[\sum_{\ell=0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}}]r_1^2 dr_1 r_2^2 dr_2 r_3^2 dr_3 \sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{+\ell} \cdot \frac{4\pi}{(2\ell+1)} \cdot$$

$$[\int_1 \int_2 \int_3 Y_2^{2^*}(1)Y_2^{2}(1)Y_2^{2^*}(2)Y_2^{2}(2)Y_2^{1^*}(3)Y_2^{1}(3) \cdot$$

$$Y_\ell^{m_\ell^*}(\theta_1,\phi_1)Y_\ell^{m_\ell}(\theta_2,\phi_2)\sin\theta_1 d\theta_1 d\phi_1 \sin\theta_2 d\theta_2 d\phi_2 \sin\theta_3 d\theta_3 d\phi_3 +$$

$$\int_1 \int_2 \int_3 Y_2^{2^*}(1)Y_2^{2}(1)Y_2^{2^*}(2)Y_2^{2}(2)Y_2^{1^*}(3)Y_2^{1}(3)Y_\ell^{m_\ell^*}(\theta_1,\phi_1)Y_\ell^{m_\ell}(\theta_3,\phi_3) \cdot$$

$$\sin\theta_1 d\theta_1 d\phi_1 \sin\theta_2 d\theta_2 d\phi_2 \sin\theta_3 d\theta_3 d\phi_3 +$$

$$\int_1 \int_2 \int_3 Y_2^{2^*}(1)Y_2^{2}(1)Y_2^{2^*}(2)Y_2^{2}(2)Y_2^{1^*}(3)Y_2^{1}(3)Y_\ell^{m_\ell^*}(\theta_2,\phi_2) \cdot$$

$$Y_\ell^{m_\ell}(\theta_3,\phi_3)\sin\theta_1 d\theta_1 d\phi_1 \sin\theta_1 d\theta_2 d\phi_2 \sin\theta_3 d\theta_3 d\phi_3] \ .$$

Which further reduces to

$$
\begin{aligned}
&\int_1\int_2\int_3 R_{3d}^*(1)R_{3d}(1)R_{3d}^*(2)R_{3d}(2)R_{3d}^*(3)R_{3d}(3)\cdot\\
&e^2\left[\sum_{\ell=0}^{\infty}\frac{r_<^{\ell}}{r_>^{\ell+1}}\right]r_1^2dr_1r_2^2dr_2r_3^2dr_3\sum_{\ell=0}^{\infty}\sum_{m_\ell=-\ell}^{+\ell}\cdot\frac{4\pi}{(2\ell+1)}\cdot\\
&\left[\int_1\int_2 Y_2^{2^*}(1)Y_2^2(1)Y_2^{2^*}(2)Y_2^2(2)Y_\ell^{m_\ell^*}(\theta_1,\phi)Y_\ell^{m_\ell}(\theta_2,\phi_2)\cdot\right.\\
&\sin\theta_1d\theta_1d\phi_1\sin\theta_2d\theta_2d\phi_2+\int_1\int_3 Y_2^{2^*}(1)Y_2^2(1)\cdot\\
&Y_2^{1^*}(3)Y_2^1(3)Y_\ell^{m_\ell^*}(\theta_1,\phi_1)Y_\ell^{m_\ell}(\theta_3,\phi_3)\sin\theta_1d\theta_1d\phi_1\cdot\\
&\sin\theta_3d\theta_3d\phi_3+\int_2\int_3 Y_2^{2^*}(2)Y_2^2(2)Y_2^{1^*}(3)Y_2^1(3)\cdot\\
&\left.Y_\ell^{m_\ell^*}(\theta_2,\phi_2)Y_\ell^{m_\ell}(\theta_3,\phi_3)\sin\theta_2d\theta_2d\phi_2\sin\theta_3d\theta_3d\phi_3\right]
\end{aligned}
$$

due to the normality of the spherical harmonics.

The product of two spherical harmonics can be expressed as a sum of spherical harmonics. Thus, we find that

$$Y_2^{2^*}Y_2^2 = Y_4^0/14\sqrt{\pi} - \sqrt{5}\ Y_2^0/7\sqrt{\pi} + Y_0^0/2\sqrt{\pi}$$

and

$$Y_2^{1^*}Y_2^1 = 2Y_4^0/7\sqrt{\pi} + \sqrt{5}\ Y_2^0/14\sqrt{\pi} + Y_0^0/2\sqrt{\pi}\quad .$$

A list of other relevant products written as sums is given in Table 7.

TABLE 7

Products of Spherical Harmonics Expressed
as Linear Combinations of
Spherical Harmonics

$$Y_2^{\pm2*}\,Y_2^{\pm2} = Y_4^{0*}/14\sqrt{\pi} - \sqrt{5}Y_2^{0*}/7\sqrt{\pi} + Y_0^{0*}/2\sqrt{\pi}$$

$$Y_2^{\pm2*}\,Y_2^{\pm1} = -\sqrt{5}Y_4^{\pm1*}/14\sqrt{\pi} + \sqrt{30}Y_2^{\pm1*}/14\sqrt{\pi}$$

$$Y_2^{\pm1*}\,Y_2^{\pm2} = \sqrt{5}Y_4^{\mp1*}/14\sqrt{\pi} - \sqrt{30}Y_2^{\mp1*}/14\sqrt{\pi}$$

$$Y_2^{\pm2*}\,Y_2^{\pm0} = Y_2^{0*}\,Y_2^{\mp2} = \sqrt{15}Y_4^{\pm2*}/14\sqrt{\pi} - \sqrt{5}Y_2^{\pm2*}/7\sqrt{\pi}$$

$$Y_2^{\pm2*}\,Y_2^{\mp1} = -\sqrt{5}Y_4^{\pm3*}/2\sqrt{7}\pi$$

$$Y_2^{\mp1*}\,Y_2^{\pm2} = \sqrt{5}Y_4^{\mp3*}/2\sqrt{7}\pi$$

$$Y_2^{\pm2*}\,Y_2^{\mp2} = \sqrt{5}Y_4^{\pm4*}/\sqrt{14}\pi$$

$$Y_2^{\pm1*}\,Y_2^{\pm1} = -2Y_4^{0*}/7\sqrt{\pi} + \sqrt{5}Y_2^{0*}/14\sqrt{\pi} + Y_0^{0*}/2\sqrt{\pi}$$

$$Y_2^{\pm1*}\,Y_2^{0} = \sqrt{30}Y_4^{\pm1*}/14\sqrt{\pi} + \sqrt{5}Y_2^{\pm1*}/14\sqrt{\pi}$$

$$Y_2^{0*}\,Y_2^{\pm1} = -\sqrt{30}Y_4^{\mp1*}/14\sqrt{\pi} - \sqrt{5}Y_2^{\mp1*}/14\sqrt{5}$$

TABLE 7--Continued

$$Y_2^{\pm1^*} Y_2^{\mp1} = -\sqrt{10}Y_4^{\pm2^*}/7\sqrt{\pi} - \sqrt{15}Y_2^{\pm2^*}/7\sqrt{2\pi}$$

$$Y_2{}^{0^*} Y_2{}^{0} = 3Y_4{}^{0^*}/7\sqrt{\pi} + \sqrt{5}Y_2{}^{0^*}/7\sqrt{\pi} + Y_0{}^{0^*}/2\sqrt{\pi}$$

Since the products $Y_2^{2^*}Y_2^{2}$ and $Y_2^{1^*}\ {}_2^{1}$ are functions of Y_4^{0}, Y_2^{0} and Y_0^{0} we need only consider in the summation those terms with $\ell = 0,2,4$ and $m_\ell = 0$. Thus, the integrals we have been considering reduce to

$$e^2\left(\frac{-7}{441}\right) \int_1 \int_2 \int_3 R_{3d}^{\ *}(1)R_{3d}(1)R_{3d}^{\ *}(2)R_{3d}(2)R_{3d}^{\ *}(3)R_{3d}(3) \cdot$$

$$\left(\frac{r_<^{\ 4}}{r_>^{\ 5}}\right)r_1^{\ 2}dr_1r_2^{\ 2}dr_2r_3^{\ 2}dr_3 \quad +$$

$$e^2\left(\frac{0}{49}\right) \cdot \int_1 \int_2 \int_3 R_{3d}^{\ *}(1)R_{3d}(1)R_{3d}^{\ *}(2)R_{3d}(2)R_{3d}^{\ *}(3)R_{3d}(3) \cdot$$

$$\left(\frac{r_<^{\ 2}}{r_>^{\ 3}}\right)r_1^{\ 2}dr_1r_2^{\ 2}dr_2r_3^{\ 2}dr_3 \quad +$$

$$e^2\left(\frac{3}{1}\right) \int_1 \int_2 \int_3 R_{3d}^{\ *}(1)R_{3d}(1)R_{3d}^{\ *}(2)R_{3d}(2)R_{3d}^{\ *}(3)R_{3d}(3) \cdot$$

$$\left(\frac{1}{r_>}\right)r_1^{\ 2}dr_1r_2^{\ 2}dr_2r_3^{\ 2}dr_3 \quad .$$

In ligand field calculations the radial integrals are not solved directly but rather defined as parameters. For the interelectronic repulsions perturbation the radial integrals become the well-known Condon and Shortly parameters. These Condon-Shortley parameters are defined as

$$F_k = \left(\frac{e^2}{D_k}\right) \int_0^\infty \int_0^\infty \int_0^\infty R_{3d}^{\ *}(1)R_{3d}^{\ *}(2)R_{3d}^{\ *}(3)R_{3d}(1)R_{3d}(2)R_{3d}(3) \quad \cdot$$

$$\left(\frac{r_<^{\ k}}{r_>^{\ k+1}}\right) \cdot r_1^{\ 2}dr_1r_2^{\ 2}dr_2r_3^{\ 2}dr_3 \quad = \quad F^k/D_k \qquad (16)$$

when $k = 0,2$ or 4 then $D_k = 1,49$ or 441, respecitvely. Therefore, the fragment of ^2H which we have been considering reduces to $3F_0 - 7F_4$. To obtain the complete energy of ^2H we must return to equation (14) and proceed as we have for the $(2\bar{2}1)$ fragment. Equation (14) reduces to

$$E'(^2H) = [6J(22) + 12J(21) - 6K(21)]/6$$

In the above expression for $E'(^2H)$ we have used the following simplified notation

$$\int_1 \int_2 (ab)(e^2/r_{12})(cd)d\tau_1 d\tau_2 = \langle(ab)|(cd)\rangle \qquad (17a)$$

$$\langle(ab)\ (cd)\rangle = \langle(cd)|(ab)\rangle^* \qquad (17b)$$

$$\langle(ab)|(ab)\rangle = J(ab) \qquad (17c)$$

$$\langle(ab)|(ba)\rangle = K(ab) \qquad (17d)$$

These integrals (17a-d) are the electron correlation integrals for d electrons. The $J(ab)$ and $K(ab)$ are known, respectively, as the Coulomb and Exchange integrals. The non-zero electron correlation integrals are listed in Table 8.

The energy of ^2H is thus

$$E'(^2H) = (F_0+4F_2+F_4) + 2(F_0-2F_2-4F_4) - (6F_2+5F_4)$$

$$E'(^2H) = 3F_0 - 6F_2 - 12F_4 \ .$$

TABLE 8

The Non-Zero Electron Correlation Integrals of the d Electrons

---

a) J(ab)

$J(\pm2\pm2)=J(\pm2\mp2)=F_0+4F_2+F_4=A+4B+2C$

$J(\pm2\pm1)=J(\pm2\mp1)=F_0-2F_2-4F_4=A-2B+C$

$J(\pm20)=F_0-4F_2+6F_4=A-4B+C$

$J(\pm1\pm1)=J(\pm1\mp1)=F_0+F_2+16F_4=A+B+2C$

$J(\pm10)=F_0+2F_2-24F_4=A+2B+C$

$J(00)=F_0+4F_2+36F_4=A+4B+3C$

---

b) K(ab)

$K(\pm2\pm1)=6F_2+5F_4=6B+C$

$K(\pm20)=4F_2+15F_4=4B+C$

$K(\pm2\mp1)=35F_4=C$

$K(\pm2\mp2)=70F_4=2C$

$K(\pm10)=F_2+30F_4=B+C$

$K(\pm1\mp1)=6F_2+40F_4=6B+2C$

---

c) <(ab)|(cd)>

$\langle(\pm2\mp2)|(\pm1\mp1)\rangle=\sqrt{6}(F_2-5F_4)=\sqrt{6}B$

$\langle(\pm2\mp1)|(\pm10)\rangle=-\sqrt{6}(F_2-5F_4)=-\sqrt{6}B$

$\langle(\pm2\mp1)|(0\pm1)\rangle=2\sqrt{6}(F_2-5F_4)=2\sqrt{6}B$

TABLE 8--*Continued*

$$\langle(\pm2\mp2)|(\pm1\mp1)\rangle=-6F_2-5F_4=-6B-C$$

$$\langle(\pm2\mp2)|(\mp1\pm1)\rangle=-35F_4=-C$$

$$\langle(\pm2\mp2)|(00)\rangle=4F_2+15F_4=4B+C$$

$$\langle(\pm1\mp1)|(00)\rangle=-F_2-30F_4=-B-C$$

$$\langle(\pm1\mp2)|(\mp10)\rangle=2\sqrt{6}(F_2-5F_4)=2\sqrt{6}B$$

$$\langle(\pm1\mp2)|(0\mp1)\rangle=-\sqrt{6}(F_2-5F_4)=-\sqrt{6}B$$

$$\langle(0\mp2)|(\mp1\mp1)\rangle=\sqrt{6}(F_2-5F_4)=\sqrt{6}B$$

We can also give the energy of ^2H with the Racah parameters A, B and C by making use of the following relationships.

$$A = F_0 - 49F_4 \,, \tag{18a}$$

$$B = F_2 - 5F_4 \qquad \text{and} \tag{18b}$$

$$C = 35F_4 \,. \tag{18c}$$

So that we have, alternatively,

$$E'(^2H) = 3A - 6B + 3C \,.$$

The energies of the other terms are calculated in the same manner. In the case of ^2D a two by two secular determinant must be solved since the cross term between ^2D-a and ^2D-b is non-zero. These interelectronic repulsions energies for the d^3 terms are given in Table 9.

In Fig. 2 the Russell-Saunders splitting is illustrated. We have omitted in this figure the A values since they are the same for each level and we are interested in energy differences. Note that ^2H and ^2P are accidentally degenerate.

The $\{L,S,X^C,X^Q\Gamma^Q\}$ Coupling Scheme

This new $\{L,S,X\}$ coupling scheme for d^3 considers the cubic and axial potentials individually, both before the spin-orbit interaction. We must now determine how the terms are affected when we lower the symmetry of the central ion by introducing the ligand field potential.

TABLE 9

The Electronic Repulsion Energies for the d^3 Terms

$^4F = 3A - 15B$

$^4P = 3A$

$^2H = 3A - 6B + 3C$

$^2G = 3A - 11B + 3C$

$^2F = 3A + 9B + 3C$

$$\begin{array}{c|cc|}
 & {}^2D\text{-}a & {}^2D\text{-}b \\ \hline
{}^2D\text{-}a & 3A+7B+7C-E_1 & 3\sqrt{21}B \\
{}^2D\text{-}b & & 3A+3B+3C-E_2
\end{array} = 0$$

$^2P = 3A - 6B + 3C$

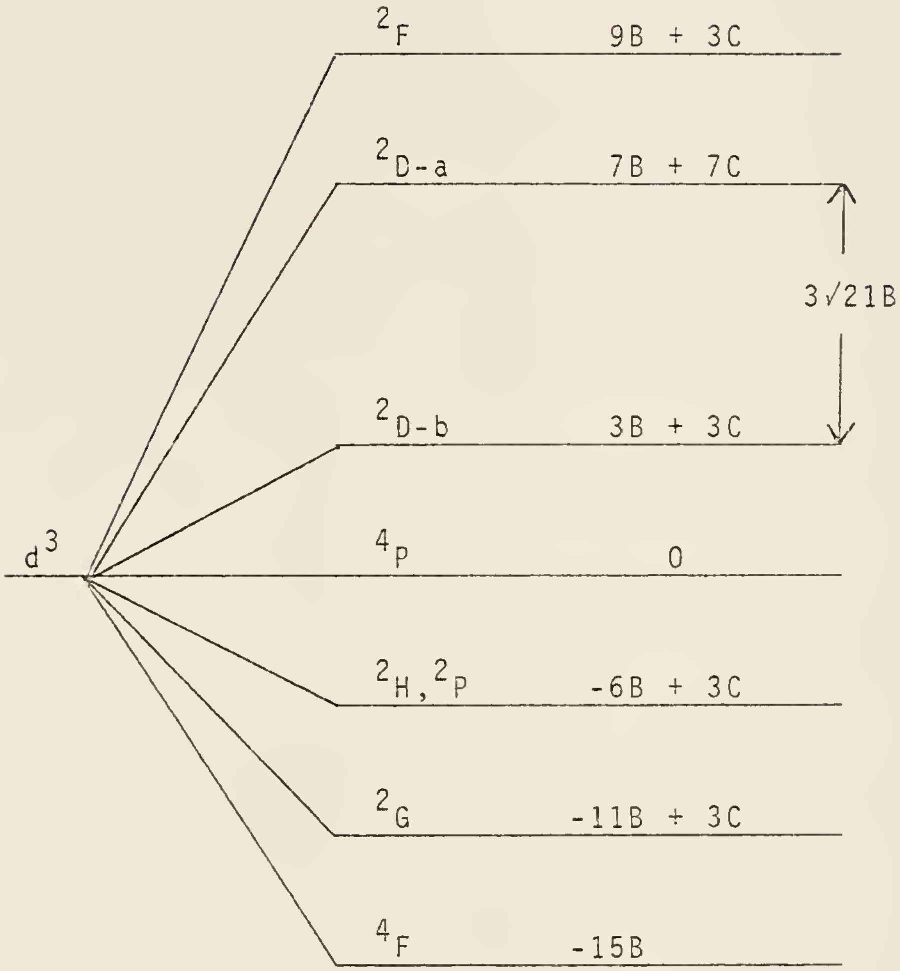

FIGURE 2. Free Ion Energy Levels for d^3

The Cubic Ligand Field

The cubic and quadrate wave functions

First we take the cubic case, that is, the octahedral arrangement of six equivalent ligands around the central ion (cf. Fig. 1). The point group for this symmetry is O_h. For O_h we have possible the following symmetry operations, grouped in classes: $3C_4$, $3C_2(=C_4^2)$, $6C_2'$, $8C_3$, E, i, and i combined with each of the previous operations. Since the d orbitals are even to inversion only the rotation operations will bring us new information.

We will assume here that the spin, ψ_s, and space, ψ_0, parts of the wave function can be separated, thus

$$\psi = \psi_0 \cdot \psi_s \tag{19}$$

and that the spin function has no angular dependence. Therefore, we need consider only the spatial part of the wave function.

For the single electron case we have the orbitals, functions of ℓ and m_ℓ, while for a many electron system we have the terms, functions of L and M_L. The angular form of the orbitals is given by

$$Y_\ell^{m_\ell} = \Theta_{\ell,m_\ell}(\theta)\sqrt{1/2\pi}\ e^{im_\ell\phi} \tag{20}$$

where $\Theta_{\ell,m_\ell}(\theta)$ are normalized, Legendre polynomials and θ and ϕ are the polar angles. Analogously, the angular dependence of the terms is

$$Y_L^{M_L} = \Theta_{L,M_L}\ \sqrt{1/2\pi}\ e^{iM_L\phi} \quad . \tag{21}$$

The relationship of the polar coordinates r, θ and ϕ with the cartesian axis x, y and z is shown in Fig. 3. Obviously, no physical quantity can depend on how we choose to locate our coordinate axis. Thus, for each of the rotation operations of O_h we can take as the axis of rotation the z axis. Clearly, θ and r are invariant to rotations about the z axis (cf. Fig. 3). So we need find only how the ϕ dependent part of the wave function, $e^{iM_L\phi}$, is affected by the various rotations.

Let us take the general case of rotation by α degrees about the z axis, $R(\alpha)$, and assume that this rotation returns the molecule to an equivalent configuration. Hence, we have

$$R(\alpha)e^{iM_L\phi} = e^{iM_L(\phi+\alpha)} \quad . \tag{22}$$

For a P term, L equals one and M_L can have the values +1, 0 and -1. Therefore, rotation by α degrees on a P term produces the following change.

$$R(\alpha) \begin{pmatrix} e^{i\phi} \\ e^{0} \\ e^{-i\phi} \end{pmatrix} = \begin{pmatrix} e^{i[\phi+\alpha]} \\ e^{0} \\ e^{-i[\phi+\alpha]} \end{pmatrix} \tag{23}$$

The same result can be obtained by multiplying the P functions by the matrix

$$\begin{pmatrix} e^{i\alpha} & 0 & 0 \\ 0 & e^{0} & 0 \\ 0 & 0 & e^{-i\alpha} \end{pmatrix} \tag{24}$$

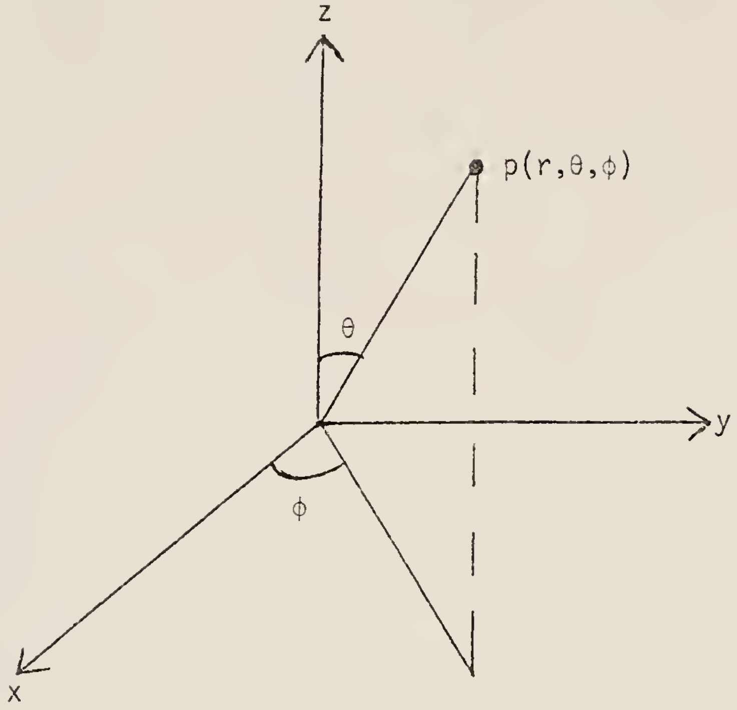

Figure 3. The Polar Coordinates r, θ and ϕ .

This matrix is the transformation matrix of the symmetry operation in question, that is, rotation by α degrees about the z axis. The set of these matrices for different rotations constitute the representation of L with the dimension $(2L+1)$.

The above result is not dependent on the value of M_L. That is, since M_L can taken all integral values between L and $-L$, we can state that the general transformation matrix which corresponds to the rotation operations of O_h is

$$\begin{pmatrix} e^{iL\alpha} & 0 & 0 & 0 & 0 \\ 0 & e^{i(L-1)\alpha} & 0 & 0 & 0 \\ \circ\circ\circ & \circ\circ\circ & \circ\circ\circ & \circ\circ\circ & \circ\circ\circ \\ 0 & 0 & 0 & e^{i(1-L)\alpha} & 0 \\ 0 & 0 & 0 & 0 & e^{-iL\alpha} \end{pmatrix} \tag{25}$$

The sum of the diagonal elements, the character of the matrix, is in the form of a geometric progression and is given by

$$\chi(\alpha) = \frac{\sin[(L+1/2)\alpha]}{\sin(\alpha/2)} \tag{26}$$

By use of (26) we can easily derive the characters corresponding to the rotation operations for different L values. It is well-known that the character of each class of a reducible representation is equal to the sum of the characters of the irreducible representations which are contained in that particular representation.

For d^3 we see that the P term yields an irreducible representation in O_h, namely T_{1g}. The D term yields a reducible representation in O_h composed of E_g and T_{2g}. The F term yields a reducible representation in O_h composed of A_{2g}, T_{1g} and T_{2g}. The G term yields a reducible representation in O_h composed of A_{1g}, Eg, T_{1g} and T_{2g}. Lastly, the H term yields a reducible representation in O_h composed of Eg, two T_{1g}'s and T_{2g}. These results for d^3 are summarized in Tables 10 and 11.

If we use directly the free-ion basis functions, i.e., the $|L,S;M_L,M_S>$ functions, to calculate the perturbation energy due to the cubic ligand field potential, we will need to solve two secular determinants, a 40x40 (for spin quartets) and an 80x80 (for spin doublets).

If the $|L,S;M_L,M_S>$ functions are linearly combined such that they are the basis functions for the irreducible representations of the cubic group then the secular determinants can be block diagonalized because of the result that the matrix elements between two different irreducible representations are zero.

The proof of the theorem on which this latter result is based follows.

Consider the following integral

$$I = \int \psi_A \psi_B \, d\tau \tag{27}$$

where ψ_A and ψ_B are functions which serve as basis functions for two irreducible representations of a group.

When we take the product of two representations of a group and, thus, obtain a third representation, the characters of the new representation will be equal to the product of the characters of the

TABLE 10

a) The Character Table of the Terms of d^3 for the Rotation Operations of O_h

L (Term)	$\chi(E)$	$\chi(C_4)$	$\chi(C_2')$	$\chi(C_3)$	$\chi(C_2)$
1 (P)	3	1	-1	0	-1
2 (D)	5	-1	1	-1	1
3 (F)	7	-1	-1	1	-1
4 (G)	9	1	1	0	1
5 (H)	11	1	-1	-1	-1

b) The Character Table of the Irreducible Representations for the Rotation Operations of O_h

Irreducible Representation	$\chi(E)$	$\chi(C_4)$	$\chi(C_2')$	$\chi(C_3)$	$\chi(C_2)$
A_{1g}	1	1	1	1	1
A_{2g}	1	-1	-1	1	1
E_g	2	0	0	-1	2
T_{1g}	3	1	-1	0	-1
T_{2g}	3	-1	1	0	-1

TABLE 11

The Splitting of the Free Ion Terms of d^3 in O_h Symmetry

Term	State(s) in O_h
^2P	$^2T_{1g}$
^2D(a and b)	$^2E_g + {}^2T_{2g}$
^2F	$^2A_{2g} + {}^2T_{1g} + {}^2T_{2g}$
^2G	$^2A_{1g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}$
^2H	$^2E_g + 2\,{}^2T_{1g} + {}^2T_{2g}$
^4P	$^4T_{1g}$
^4F	$^4A_{2g} + {}^4T_{1g} + {}^4T_{2g}$

two representations that were multiplied together to give the new representation. That is, if the product of representations A and B is C, then

$$\chi_C = \chi_A \cdot \chi_B \tag{28}$$

for each class. This is known as the direct product of the representations A and B.

We have assumed that ψ_A and ψ_B are bases for irreducible representations of a group. The product of two irreducible representations may or may not be irreducible. If ψ_A transforms as Γ_A and ψ_B as Γ_B where Γ_A and Γ_B are irreducible representations of our group, then

$$\Gamma_A \cdot \Gamma_B = \Gamma_C = \sum_i C_i \Gamma_i \tag{29}$$

If Γ_C is reducible, then $\sum_i C_i \Gamma_i$ is the sum of irreducible representations which compose Γ_C.

Let us operate on I with one of the operations, R, of the group to which Γ_A and Γ_B belong. The value of any integral will be just a number which will not be changed by a symmetry operation. That is

$$RI = IR = I \ , \tag{30}$$

further

$$I = \int R\psi_A\psi_B d\tau = \int R\Gamma_A \cdot \Gamma_B d\tau \ , \qquad \text{or}$$

$$I = \int R\sum_i C_i \Gamma_i d\tau \ . \tag{31}$$

Since the value of the integral does not change when we apply a symmetry operation to it, i.e., RI = I, then the form of the integral, $\int\sum_i C_i\Gamma_i d\tau$, must also be invariant under all the symmetry operations of the group. This will be so only when one of the Γ_i is the totally symmetric representation A_1. This is the case because A_1 is the sole representation that is invariant under all the symmetry operations of the group.

For the product $\Gamma_A \cdot \Gamma_B$ to contain the totally symmetric representation, Γ_A and Γ_B must be identical. That is $\Gamma_A \equiv \Gamma_B$.

Therefore, we can conclude that integrals of the form

$$\int \psi_A \psi_B \, d\tau$$

can be non-zero only when the representations Γ_A and Γ_B, for which ψ_A and ψ_B serve as basis functions, are identical.

The matrix elements have the familiar form of

$$H_{ij} = \int \psi_i^* H' \psi_j \, d\tau = \langle i|H'|j\rangle \quad . \tag{32}$$

The Hamiltonian, of which H' is part, is an expression, in quantum mechanical operator form, of the energy of a system. Application of a symmetry operation of a molecule cannot change the energy of a molecule and all symmetry operations will leave the Hamiltonian invariant. The Hamiltonian operator thus belongs to the totally symmetric representation A_1. The integral $\int \psi_i^* H' \psi_j \, d\tau$ can therefore be non-zero only if the direct product $\Gamma_i\Gamma_j$ contains A_1 and, as we have observed, this only occurs when $\Gamma_i = \Gamma_j$. Hence, the matrix elements can be non-zero only if the wavefunctions ψ_i and ψ_j belong to the same irreducible representation.

For the d^3 cubic case the secular determinant is thus block diagonalized as shown in Fig. 4.

Our aim then is to find the linear combinations of the free-ion functions which serve as the basis functions of the various irreducible representations. The $|L,S;M_L,M_S>$ functions have the same angular dependence as the spherical harmonics and these $|L,M_L>$ functions that serve as the bases for the irreducible representations of the cubic group are the cubic oriented spherical harmonics.

To illustrate the formation of the cubic oriented spherical harmonics we shall take the P term as an example. From Fig. 3 it is easy to see that the cartesian coordinates relate to the polar coordinates as follows:

$$z = r\cos\theta, \tag{33a}$$

$$y = r\sin\theta\sin\phi \quad \text{and} \tag{33b}$$

$$x = r\sin\theta\cos\phi\ . \tag{33c}$$

Thus, we can write the spherical harmonics for a P term as a function of x, y and z. We obtain

$$Y_1^{-1} = \sqrt{3/8\pi}\,(x-iy)/r\ , \tag{34a}$$

$$Y_1^{0} = \sqrt{3/4\pi}\,z/r \quad \text{and} \tag{34b}$$

$$Y_1^{1} = -\sqrt{3/8\pi}\,(x+iy)/r\ . \tag{34c}$$

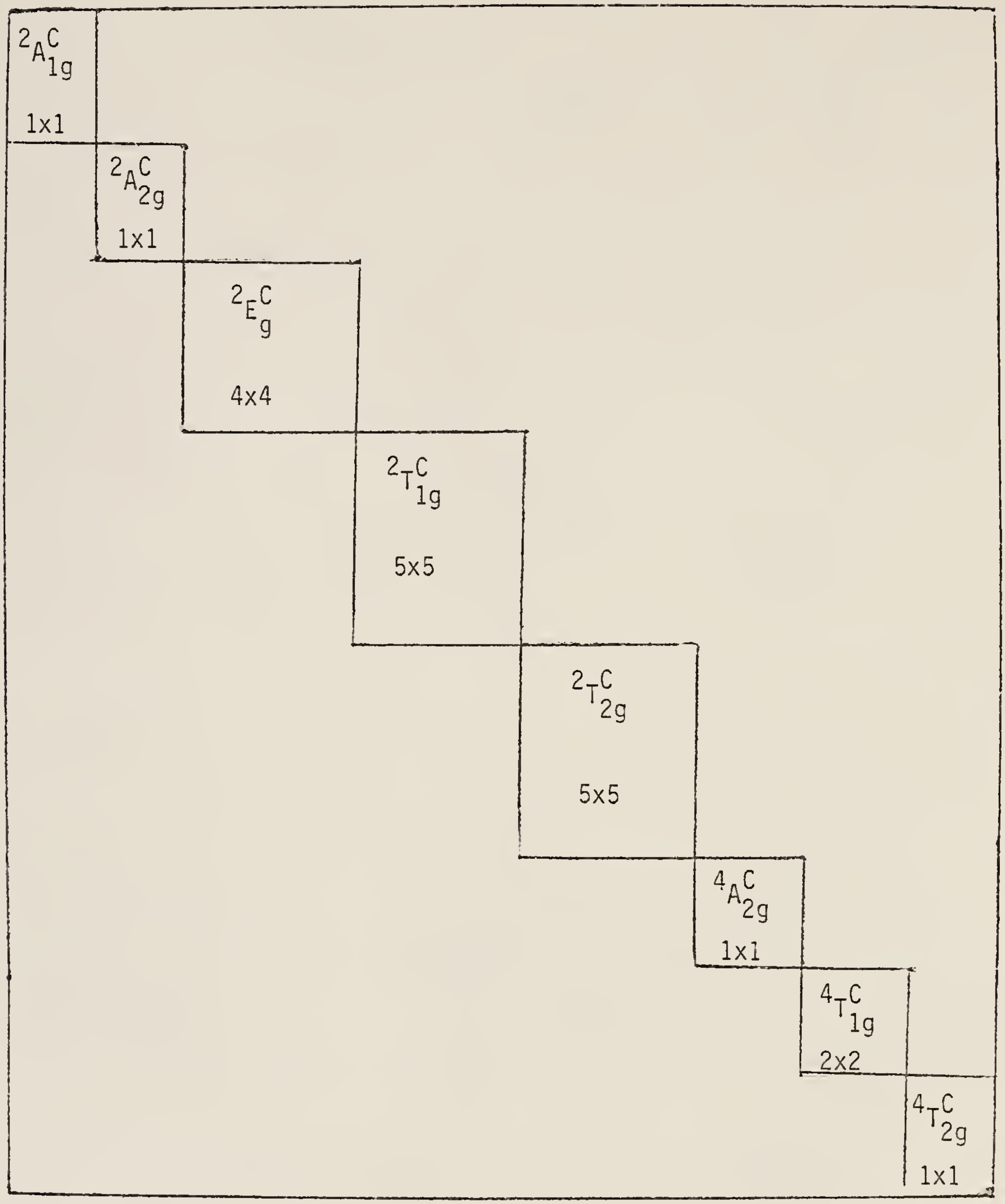

Figure 4. The cubic secular determinant for d^3 for the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme.

Our phases will agree with those of Condon and Shortley,[1] i.e., the spherical harmonics with m_ℓ odd and positive are given a minus sign.

The real forms of these spherical harmonics correspond to the following combinations:

$$z \sim Y_1^{0} , \tag{35a}$$

$$y \sim i(Y_1^{-1}+Y_1^{1})/\sqrt{2} \quad \text{and} \tag{35b}$$

$$x \sim (Y_1^{-1}-Y_1^{1})/\sqrt{2} . \tag{35c}$$

These are known as the "p-orbitals" in the case of a single electron and have the same symmetry properties as z,y and x.

Let us examine how these cartesian functions z,y and x will be affected by the rotation operations of O_h symmetry. We will take the z axis as the principal rotation axis, i.e., $C_4(z)$. The other rotations, each representing a class, are $C_2 \equiv C_4^{2}(z)$, a C_2 colinear with the y axis which we shall call $C_2'(y)$, the threefold body diagonal rotation $C_3(z')$ and, of course, the identity operation E. Using counter clockwise rotations and "replaced by" operations, the transformation properties of z,y and x are given below.

$$\begin{pmatrix} z \\ y \\ x \end{pmatrix} \xrightarrow{\quad C_4(z) \quad} \begin{pmatrix} z \\ x \\ -y \end{pmatrix} \tag{36a}$$

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[1] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, University Press, Cambridge, 1951.

$$\begin{pmatrix} z \\ y \\ x \end{pmatrix} \underline{\qquad C_2 \equiv C_4{}^2(z) \qquad} \begin{pmatrix} z \\ -y \\ -x \end{pmatrix} \tag{36b}$$

$$\begin{pmatrix} z \\ y \\ x \end{pmatrix} \underline{\qquad\quad C_2{}'(y) \qquad\quad} \begin{pmatrix} -z \\ y \\ -x \end{pmatrix} \tag{36c}$$

$$\begin{pmatrix} z \\ y \\ x \end{pmatrix} \underline{\qquad\quad C_3(z') \qquad\quad} \begin{pmatrix} y \\ x \\ z \end{pmatrix} \tag{36d}$$

$$\begin{pmatrix} z \\ y \\ x \end{pmatrix} \underline{\qquad\qquad E \qquad\qquad} \begin{pmatrix} z \\ y \\ x \end{pmatrix} \tag{36e}$$

The matrices which will accomplish the above transformations when applied to $\begin{pmatrix} z \\ y \\ x \end{pmatrix}$ are listed in Table 12 underneath the appropriate symmetry operations. These matrices constitute a representation of the basis functions z,y and x. The characters of each matrix are also given in Table 12. By referring back to Table 10(b) we see that z,y and x form a basis for the irreducible representation T_{1g} of O_h symmetry.

Since z,y and x form a basis for the irreducible representation T_{1g}, we can use the real forms of the spherical harmonics which correspond to z,y and x, i.e., (28), as the wave functions for the triply degenerate T_{1g} representation that arises from P. These are the cubic oriented spherical harmonics for $L = 1$.

TABLE 12

Matrices and Characters of the Representation Spanned by (z,y,x) in O_h Symmetry

	E	$C_4(z)$	$C_2 \equiv C_4{}^2(z)$	$C_2{}^1(y)$	$C_3(z')$
(z,y,x)	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$
$\chi(R)$	3	1	-1	-1	0

Immediately, the question arises as to which is the a, b and c component of $T_{1g}{}^C(P)$. Though the choice is completely arbitrary it is important that the convention chosen is adhered to strictly in all the following calculations.

First, let us see how the T_{1g} representation decomposes when the symmetry is lowered to tetragonal. It is necessary to consider this now because it will play a role in our choosing of the a, b and c components of T_{1g}.

Here, we need to consider only those rotations that are common to O_h and D_{4h}. These are the $C_4(z)$, $C_2 \equiv C_4{}^2(z)$, $C_2{}'(y)$ and E. It is obvious that the transformation properties of z,y and x will not differ in going from O_h to D_{4h} for these operations. But the representation spanned by them may not be irreducible in D_{4h}. The characters for the basis (z,y,x) and for the irreducible representations of D_{4h} for the operations we are dealing with are compared in Table 13.

TABLE 13

Character Table for the Representation for Which (z,y,x) is a Basis in D_{4h} and for the Irreducible Representations of D_{4h}

	$\chi(E)$	$\chi(C_4)$	$\chi(C_2)$	$\chi(C_2')$
(z,y,x)	3	1	-1	-1
A_{1g}	1	1	1	1
A_{2g}	1	1	1	-1
B_{1g}	1	-1	1	1
B_{2g}	1	-1	1	-1
E_g	2	0	-2	0

The cartesian axes, (z,y,x), do not form a basis for an irreducible representation in D_{4h}. This is obvious since D_{4h} has no representation of dimension greater than two. Decomposing we find (z,y,x) is composed of A_{2g} and E_g.

Reviewing the transformation properties of z in D_{4h} (cf. equns. 36a-c), which are the same as those in O_h for the rotations common to the two point groups, we see that z always transforms as plus or minus of itself while y and x mix. This indicates that z alone is the basis for the singly degenerate A_{2g} representation and (y,x) together form the basis for the doubly degenerate E_g representation. This is easily confirmed by comparing the characters of z and (y,x) with those of A_{2g} and E_g under the rotations of D_{4h}.

Now we can state our convention for choosing the a, b and c components of T_{1g}. First we choose z as the basis for the a component of T_{1g}. Thus, when the symmetry is lowered to D_{4h} we have

$$T^C_{1ga} \rightarrow A^Q_{2g} .$$

Next we decide that under $C_3(z')$ of O_h a will be replaced by b, b by c, and c by a. From (29d) we see that $C_3(z')$ replaces z by y, y by x and x by z. Hence, y and x become the b and c components, respectively, of T_{1g}. Further, we specify that the b component of T_{1g} becomes the a component of E_g and the c component of T_{1g} becomes the b component of E_g when the symmetry is lowered to tetragonal.

That is

$$T^C_{1gb} \rightarrow E^Q_{ga} \qquad \text{and}$$

$$T^C_{1gc} \rightarrow E^Q_{gb} .$$

Finally, in Table 14 below we have summarized the wave functions, the real forms of the spherical harmonics, for T_{1g} from P and the decomposition properties of T_{1g} when the symmetry is lowered to tetragonal.

TABLE 14

Wave Functions and Decomposition
Properties of $T^{C}_{1g}(P)$

Wave Function	Cartesian Representation	O_h Representation	D_{4h} Representation
Y_1^{0}	z	T^{C}_{1ga}	A^{Q}_{2g}
$i(Y_1^{-1}+Y_1^{1})/\sqrt{2}$	y	T^{C}_{1gb}	E^{Q}_{ga}
$(Y_1^{-1}-Y_1^{1})/\sqrt{2}$	x	T^{C}_{1gc}	E^{Q}_{gb}

The wave functions and decomposition of the other terms are found in exactly the same manner. A complete list of the cubic oriented spherical harmonics corresponding to the cubic irreducible representations of all the d^3 terms is given in Table 15. We have used the shorthand notation $|L,M_L>$ for the spherical harmonics in Table 15.

In Table 16 the decomposition of the cubic levels ingoing to D_{4h} is given.

To obtain the cubic oriented spherical harmonics in microstate form one inserts the $|L,S;M_L,M_S>$ functions (cf. Table 6) for each corresponding $|L,M_L>$ spherical harmonic. We choose the maximum M_S for each $|L,S;M_L,M_S>$ function which is to be substituted for $|L,M_L>$'s in writing down the cubic oriented spherical harmonics in microstate form. The cubic oriented spherical harmonics in microstate form are listed in Table 17.

TABLE 15

The Cubic Oriented Spherical Harmonics for the d^3 Terms

Term	O_h Level	Cartesian Representation[j]	Wave Function[k]
$^{2\text{ or }4}P$	$^{2\text{ or }4}T_{1ga}$	z	$\|1,0\rangle$
	$^{2\text{ or }4}T_{1gb}$	y	$i(\|1,-1\rangle+\|1,1\rangle)/\sqrt{2}$
	$^{2\text{ or }4}T_{1gc}$	x	$(\|1,-1\rangle-\|1,1\rangle)/\sqrt{2}$
^2D(a or b)	$^2E_{ga}$	$(3z^2-r^2)/2\sqrt{3}$	$\|2,0\rangle$
	$^2E_{gb}$	$(x^2-y^2)/2$	$(\|2,2\rangle+\|2,-2\rangle)/\sqrt{2}$
	$^2T_{2ga}$	xy	$i(\|2,-2\rangle-\|2,2\rangle)/\sqrt{2}$
	$^2T_{2gb}$	xz	$(\|2,-1\rangle-\|2,1\rangle)/\sqrt{2}$
	$^2T_{2gc}$	yz	$i(\|2,-1\rangle+\|2,1\rangle)/\sqrt{2}$

TABLE 15--Continued

Term	O_h Level	Cartesian Representation[j]	Wave Function[k]
2 or ^4F	2 or $^4A_{2g}^{C}$	xyz	$i(\|3,-2\rangle-\|3,2\rangle)/\sqrt{2}$
	2 or $^4T_{1ga}$	$\sqrt{5}/12z(z^2-3r^2/5)$	$\|3,0\rangle$
	2 or $^4T_{1gb}$	$\sqrt{5}/12y(y^2-3r^2/5)$	$-i(\sqrt{3}(\|3,1\rangle+\|3,-1\rangle)+\sqrt{5}(\|3,3\rangle+\|3,-3\rangle))/4$
	2 or $^4T_{1gc}$	$\sqrt{5}/12x(x^2-3r^2/5)$	$(\sqrt{3}(\|3,1\rangle-\|3,-1\rangle)+\sqrt{5}(\|3,-3\rangle-\|3,3\rangle))/4$
	2 or $^4T_{2ga}$	$z(x^2-y^2)/2$	$(\|3,2\rangle+\|3,-2\rangle)/\sqrt{2}$
	2 or $^4T_{2gb}$	$y(z^2-x^2)/2$	$i(\sqrt{5}(\|3,1\rangle+\|3,-1\rangle)-\sqrt{3}(\|3,3\rangle+\|3,-3\rangle))/4$
	2 or $^4T_{2gc}$	$x(y^2-z^2)/2$	$(\sqrt{5}(\|3,1\rangle-\|3,-1\rangle)+\sqrt{3}(\|3,-3\rangle-\|3,3\rangle))/4$
^2G	$^2A_{1g}$	$\sqrt{105}(x^4+y^4+z^4-3r^4/5)$	$(\sqrt{14}\|4,0\rangle+\sqrt{5}\|4,4\rangle+\sqrt{5}\|4,-4\rangle)/\sqrt{24}$
	$^2E_{ga}$	$(2z^4-x^4-y^4-(6/7)(3z^2-r^2))/2$	$(\sqrt{10}\|4,0\rangle-\sqrt{7}\|4,4\rangle-\sqrt{7}\|4,-4\rangle)/\sqrt{24}$

TABLE 15--Continued

Term	O_h Level	Cartesian Representation[j]	Wave Function[k]
	$^2E_{gb}$	$(x^4-y^4-(6/7)r^2(x^2-y^2))/2$	$-(\|4,2\rangle+\|4,-2\rangle)/\sqrt{2}$
	$^2T_{1ga}$	$xy(x^2-y^2)/\sqrt{7}$	$i(\|4,-4\rangle-\|4,4\rangle)/\sqrt{2}$
	$^2T_{1gb}$	$xz(z^2-x^2)/\sqrt{7}$	$(\sqrt{7}\|4,-1\rangle-\sqrt{7}\|4,1\rangle+\|4,3\rangle-\|4,-3\rangle)/4$
	$^2T_{1gc}$	$yz(y^2-z^2)/\sqrt{7}$	$-i(\sqrt{7}\|4,-1\rangle+\sqrt{7}\|4,1\rangle+\|4,3\rangle+\|4,-3\rangle)/4$
	$^2T_{2ga}$	$xy(z^2-r^2/7)$	$i(\|4,-2\rangle-\|4,2\rangle)/\sqrt{2}$
	$^2T_{2gb}$	$xz(y^2-r^2/7)$	$(\|4,1\rangle-\|4,-1\rangle+\sqrt{7}\|4,3\rangle-\sqrt{7}\|4,-3\rangle)/4$
	$^2T_{2gc}$	$yz(x^2-r^2/7)$	$-i(\|4,1\rangle+\|4,-1\rangle-\sqrt{7}\|4,3\rangle-\sqrt{7}\|4,-3\rangle)/4$
^2H	$^2E_{ga}$	$\sqrt{15}xyz(x^2-y^2)$	$i(\|5,-4\rangle-\|5,4\rangle)/\sqrt{2}$
	$^2E_{gb}$	$-\sqrt{5}xyz(2z^2-x^2-y^2)$	$i(\|5,2\rangle-\|5,-2\rangle)/\sqrt{2}$

TABLE 15--Continued

Term	O_h Level	Cartesian Representation[j]	Wave Function[k]
	$^2T_{1ga}$-1	$\sqrt{189}(z^5-10zr^2(z^2-3r^2/5)/9-3zr^4/7)/4$	$|5,0\rangle$
	$^2T_{1gb}$-1	$\sqrt{189}(y^5-10yr^2(y^2-3r^2/5)-3yr^4/7)/4$	$i(3\sqrt{7}(|5,-5\rangle+|5,5\rangle)+\sqrt{35}(|5,-3\rangle+|5,3\rangle)$ $+\sqrt{30}(|5,-1)+|5,1\rangle))/16$
	$^2T_{1gc}$-1	$\sqrt{189}(x^5-10xr^2(x^2-3r^2/5)-3xr^4/7)/4$	$(3\sqrt{7}(|5,-5\rangle-|5,5\rangle)+\sqrt{35}(|5,3\rangle-\sqrt{5},-3\rangle)$ $+\sqrt{30}(|5,-1\rangle-|5,1\rangle))/16$
	$^2T_{1ga}$-2	$\sqrt{15}(z(x^4+y^4-3(x^2+y^2)^2/4)$	$(|5,4\rangle+|5,-4\rangle)/\sqrt{2}$
	$^2T_{1gb}$-2	$\sqrt{15}(y(x^4+z^4-3(x^2+z^2)^2/4))$	$i(\sqrt{5}(|5,-5\rangle+|5,5\rangle)-9(|5,-3\rangle+|5,3\rangle)$ $+\sqrt{42}(|5,-1\rangle+|5,1\rangle))/16$
	$^2T_{1gc}$-2	$\sqrt{15}(x(y^4+z^4-3(y^2+z^2)^2/4))$	$(\sqrt{5}(|5,-5\rangle-|5,5\rangle)+9(|5,-3\rangle-|5,3\rangle)$ $+\sqrt{42}(|5,-1\rangle-|5,1\rangle))/16$
	$^2T_{2ga}$	$\sqrt{45}(z(z^2-r^2/3)\cdot(x^2-y^2))/2$	$(|5,2\rangle+|5,-2\rangle)/\sqrt{2}$

TABLE 15--Continued

Term	O_h Level	Cartesian Representation[j]	Wave Function[k]
	$^2T_{2gb}$	$\sqrt{45}(y(y^2-r^2/3)\cdot(z^2-x^2))/2$	$i(\sqrt{15}(\vert 5,-5\rangle+\vert 5,5\rangle)-\sqrt{3}(\vert 5,-3\rangle+\vert 5,3\rangle)$ $-\sqrt{14}(\vert 5,-1\rangle+\vert 5,1\rangle))/8$
	$^2T_{2gc}$	$\sqrt{45}(x(x^2-r^2/3)\cdot(y^2-z^2))/2$	$(\sqrt{15}(\vert 5,5\rangle-\vert 5,-5\rangle)+\sqrt{3}(\vert 5,3\rangle-\vert 5,-3\rangle)$ $+\sqrt{14}(\vert 5,-1\rangle-\vert 5,1\rangle))/8$

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[j] The common factors of $\sqrt{3/4\pi}$, $\sqrt{15/4\pi}$, $\sqrt{105/4\pi}$, $105/\sqrt{160\pi}$, and $\sqrt{331}/16\pi$ for p, d, f, g and h, respectively, have been omitted in this column.

[k] These cubic oriented spherical harmonics are taken from a set of unpublished notes. The notes, entitled "The Colors of Mn(II) and Fe(III) Compounds", were written by A.D. Liehr.

TABLE 16

Decomposition of the Cubic Representations in Going to Tetragonal Symmetry

Cubic Representation	Tetragonal Representation
A_{1g}	A_{1g}
A_{2g}	B_{1g}
E_{ga}	A_{1g}
E_{gb}	B_{1g}
T_{1ga}	A_{2g}
T_{1gb}	E_{ga}
T_{1gc}	E_{gb}
T_{2ga}	B_{2g}
T_{2gb}	E_{ga}
T_{2gc}	E_{gb}

TABLE 17

The Cubic Oriented Spherical Harmonics in Microstate Form for the d^3 Terms

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^2P

$$\begin{aligned} {}^2T^C_{1ga} = {}^2A^Q_{2g} &= (-4(20-\bar{2})-3\sqrt{6}(1\bar{1}-2)+8(2\bar{0}-2)-4(\bar{2}0-2) \\ &\quad -(10-\bar{1})+3\sqrt{6}(2-1-\bar{1})+2(1\bar{0}-1)-(\bar{1}0-1))/\sqrt{210} \end{aligned}$$

$$\begin{aligned} {}^2T^C_{1gb} = {}^2E^Q_{ga} &= i(-4\sqrt{3}(21-\bar{2})+2\sqrt{3}(2\bar{1}-2)+2\sqrt{3}(\bar{2}1-2) \\ &\quad +4\sqrt{2}(20-\bar{1})+\sqrt{2}(2\bar{0}-1)-5\sqrt{2}(\bar{2}0-1)-3\sqrt{3}(1\bar{1}-1)-3\sqrt{3}(10\bar{0}) \\ &\quad +2\sqrt{3}(2-1-\bar{2})-5\sqrt{2}(10-\bar{2})+4\sqrt{2}(\bar{1}0-2)+\sqrt{2}(1\bar{0}-2)+2\sqrt{3}(2-\bar{1}-2) \\ &\quad -4\sqrt{3}(\bar{2}-1-2)+3\sqrt{3}(1-1-\bar{1})+3\sqrt{3}(0\bar{0}-1))/\sqrt{420} \end{aligned}$$

$$\begin{aligned} {}^2T^C_{1gc} = {}^2E^Q_{gb} &= (4\sqrt{3}(21-\bar{2})-2\sqrt{3}(2\bar{1}-2)-2\sqrt{3}(\bar{2}1-2) \\ &\quad -4\sqrt{2}(20-\bar{1})-\sqrt{2}(2\bar{0}-1)+5\sqrt{2}(\bar{2}0-1)+3\sqrt{3}(1\bar{1}-1)+3\sqrt{3}(10\bar{0}) \\ &\quad +2\sqrt{3}(2-1-\bar{2})-5\sqrt{2}(10-\bar{2})+4\sqrt{2}(\bar{1}0-2)+\sqrt{2}(1\bar{0}-2)+2\sqrt{3}(2-\bar{1}-2) \\ &\quad -4\sqrt{3}(\bar{2}-1-2)+3\sqrt{3}(1-1-\bar{1})+3\sqrt{3}(0\bar{0}-1))/\sqrt{420} \end{aligned}$$

$^2D\text{-}a$

$$ {}^2E^C_{ga} = {}^2A^Q_{1g} = ((10-\bar{1})+(\bar{2}0-2)-(\bar{1}0-1)-(20-\bar{2}))/2 $$

$$\begin{aligned} {}^2E^C_{gb} = {}^2B^Q_{1g} &= ((2\bar{1}-1)+(20\bar{0})-(2\bar{2}-2)-(21-\bar{1})+(\bar{1}-1-2) \\ &\quad +(0\bar{0}-2)-(2-2-\bar{2})-(1-\bar{1}-2))/\sqrt{8} \end{aligned}$$

$$\begin{aligned} {}^2T^C_{2ga} = {}^2B^Q_{2g} &= i((\bar{1}-1-2)+(0\bar{0}-2)-(2-2-\bar{2})-(1-\bar{1}-2) \\ &\quad -(2\bar{1}-1)-(20\bar{0})+(2\bar{2}-2)+(21-\bar{1}))/\sqrt{8} \end{aligned}$$

TABLE 17--Continued

$$\begin{aligned}{}^2T^C_{2gb} = {}^2E^Q_{ga} &= ((1\text{-}1\text{-}\bar{1})+(\bar{2}\text{-}1\text{-}2)+(0\bar{0}\text{-}1)-(2\text{-}1\text{-}\bar{2})-(1\bar{1}\text{-}1)\\ &- (10\bar{0})-(\bar{2}1\text{-}2)+(21\text{-}\bar{2}))/\sqrt{8}\end{aligned}$$

$$\begin{aligned}{}^2T^C_{2gc} = {}^2E^Q_{gb} &= i((1\text{-}1\text{-}\bar{1})+(\bar{2}\text{-}1\text{-}2)+(0\bar{0}\text{-}1)-(2\text{-}1\text{-}\bar{2})+(1\bar{1}\text{-}1)\\ &+ (10\bar{0})+(\bar{2}1\text{-}2)-(21\text{-}\bar{2}))/\sqrt{8}\end{aligned}$$

${}^2\text{D-b}$

$$\begin{aligned}{}^2E^C_{ga} = {}^2A^Q_{1g} &= (3(20\text{-}\bar{2})-2\sqrt{6}(1\bar{1}\text{-}2)-3(\bar{2}0\text{-}1)-3(\bar{1}0\text{-}1)\\ &+ 3(10\text{-}\bar{1})-2\sqrt{6}(2\text{-}1\text{-}\bar{1}))/\sqrt{84}\end{aligned}$$

$$\begin{aligned}{}^2E^C_{gb} = {}^2B^Q_{1g} &= (4(1\text{-}1\text{-}\bar{2})-5(2\text{-}2\text{-}\bar{2})-3(0\bar{0}\text{-}2)-(1\text{-}\bar{1}\text{-}2)-3(\bar{1}\text{-}1\text{-}2)\\ &- 2\sqrt{6}(0\text{-}1\text{-}\bar{1})+3(21\text{-}\bar{1})-5(2\bar{2}\text{-}2)+(2\bar{1}\text{-}1)-4(\bar{2}1\text{-}1)-3(20\bar{0})\\ &- 2\sqrt{6}(1\bar{1}0))/2\sqrt{42}\end{aligned}$$

$$\begin{aligned}{}^2T^C_{2ga} = {}^2B^Q_{2g} &= i(4(1\text{-}1\text{-}\bar{2})-5(2\text{-}2\text{-}\bar{2})-3(0\bar{0}\text{-}2)-(1\text{-}\bar{1}\text{-}2)\\ &- 3(\bar{1}\text{-}1\text{-}2)-2\sqrt{6}(0\text{-}1\text{-}\bar{1})-3(21\text{-}\bar{1})+5(2\bar{2}\text{-}2)-(2\bar{1}\text{-}1)+4(\bar{2}1\text{-}1)\\ &+ 3(20\bar{0})+2\sqrt{6}(1\bar{1}0))/2\sqrt{42}\end{aligned}$$

$$\begin{aligned}{}^2T^C_{2gb} = {}^2E^Q_{ga} &= (2\sqrt{6}(10\text{-}\bar{2})-(2\text{-}1\text{-}\bar{2})-2\sqrt{6}(1\bar{0}\text{-}2)-3(\bar{2}\text{-}1\text{-}2)\\ &+ 3(0\bar{0}\text{-}1)-(1\text{-}1\text{-}\bar{1})+4(2\text{-}\bar{1}\text{-}2)-3(21\text{-}\bar{2})-(\bar{2}1\text{-}2)+4(2\bar{1}\text{-}2)\\ &+ (1\bar{1}\text{-}1)-3(10\bar{0})+2\sqrt{6}(\bar{2}0\text{-}1)-2\sqrt{6}(2\bar{0}\text{-}1))/2\sqrt{42}\end{aligned}$$

$$\begin{aligned}{}^2T^C_{2gc} = {}^2E^Q_{gb} &= i(2\sqrt{6}(10\text{-}\bar{2})-(2\text{-}1\text{-}\bar{2})-2\sqrt{6}(1\bar{0}\text{-}2)\\ &- 3(\bar{2}\text{-}1\text{-}2)+3(0\bar{0}\text{-}1)-(1\text{-}1\text{-}\bar{1})+4(2\text{-}\bar{1}\text{-}2)+3(21\text{-}\bar{2})+(\bar{2}1\text{-}2)\\ &- 4(2\bar{1}\text{-}2)-(1\bar{1}\text{-}1)+3(10\bar{0})-2\sqrt{6}(\bar{2}0\text{-}1)+2\sqrt{6}(2\bar{0}\text{-}1))/2\sqrt{42}\end{aligned}$$

TABLE 17--Continued

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^2F

$$\begin{aligned}
{}^2A^C_{2g} = {}^2B^Q_{1g} &= i(\sqrt{6}(0-1-\bar{1})+(1-\bar{1}-2)-2(2-2-\bar{2})-(\bar{1}-1-2)\\
&- (2\bar{1}-1)-2(2\bar{2}-2)+\sqrt{6}(1\bar{1}0)+(21-\bar{1}))/2\sqrt{6}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{1ga} = {}^2A^Q_{2g} &= (2(\bar{1}0-1)-4(1\bar{0}-1)+\sqrt{6}(1\bar{1}-2)-\sqrt{6}(2-1-\bar{1})\\
&+ 4(2\bar{0}-2)-2(\bar{2}0-2)+2(10-\bar{1})-2(20-\bar{2}))/\sqrt{60}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{1gb} = {}^2E^Q_{ga} &= -i(-2\sqrt{6}(1\bar{1}-1)+3(2\bar{0}-1)+3\sqrt{6}(2\bar{1}-2)-2\sqrt{6}(\bar{2}1-2)\\
&+ 3\sqrt{6}(10\bar{0})-3(20-\bar{1})-\sqrt{6}(21-\bar{2})+2\sqrt{6}(1-1-\bar{1})-3\sqrt{6}(0\bar{0}-1)-3(\bar{1}0-2)\\
&+ 3(1\bar{0}-2)+3\sqrt{6}(2-\bar{1}-2)-2\sqrt{6}(2-1-\bar{2})-\sqrt{6}(\bar{2}-1-2)+10(0-1-\bar{2})\\
&- 5(0-\bar{1}-2)-5\sqrt{6}(1-2-\bar{2})-5(\bar{0}-1-2)+5\sqrt{6}(2\bar{2}-1)+10(\bar{2}10)\\
&- 5(21\bar{0})-5(2\bar{1}0))/8\sqrt{15}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{1gc} = {}^2E^Q_{gb} &= (-2\sqrt{6}(1\bar{1}-1)+3(2\bar{0}-1)+3\sqrt{6}(2\bar{1}-2)-2\sqrt{6}(\bar{2}1-2)\\
&+ 3\sqrt{6}(10\bar{0})-3(20-\bar{1})-\sqrt{6}(21-\bar{2})-2\sqrt{6}(1-1-\bar{1})+3\sqrt{6}(0\bar{0}-1)\\
&+ 3(\bar{1}0-2)-3(1\bar{0}-2)-3\sqrt{6}(2-\bar{1}-2)+2\sqrt{6}(2-1-\bar{2})+\sqrt{6}(\bar{2}-1-2)\\
&+ 10(0-1-\bar{2})-5(0-\bar{1}-2)-5\sqrt{6}(1-2-\bar{2})-5(\bar{0}-1-2)-5\sqrt{6}(2\bar{2}-1)\\
&- 10(\bar{2}10)+5(21\bar{0})+5(2\bar{1}0))/8\sqrt{15}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{2ga} = {}^2B^Q_{2g} &= ((2\bar{1}-1)+2(2\bar{2}-2)-\sqrt{6}(1\bar{1}0)-(21-\bar{1})+\sqrt{6}(0-1-\bar{1})\\
&+ (1-\bar{1}-2)-2(2-2-\bar{2})-(\bar{1}-1-2))/2\sqrt{6}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{2gb} = {}^2E^Q_{ga} &= i(-2\sqrt{2}(1\bar{1}-1)+\sqrt{3}(2\bar{0}-1)+3\sqrt{2}(2\bar{1}-2)-2\sqrt{2}(\bar{2}1-2)\\
&+ 3\sqrt{2}(10\bar{0})-\sqrt{3}(20-\bar{1})-\sqrt{2}(21-\bar{2})+2\sqrt{2}(1-1-\bar{1})-3\sqrt{2}(0\bar{0}-1)\\
&- \sqrt{3}(\bar{1}0-2)+\sqrt{3}(1\bar{0}-2)+3\sqrt{2}(2-\bar{1}-2)-2\sqrt{}(2-1-\bar{2})\\
&- \sqrt{2}(\bar{2}-1-2)-2\sqrt{3}(0-1-\bar{2})+\sqrt{3}(0-\bar{1}-2)+3\sqrt{2}(1-2-\bar{2})+\sqrt{3}(\bar{0}-1-2)\\
&- 3\sqrt{2}(2\bar{2}-1)-2\sqrt{3}(\bar{2}10)+\sqrt{3}(21\bar{0})+\sqrt{3}(2\bar{1}0))/4\sqrt{12}
\end{aligned}$$

TABLE 17--Continued

$$
\begin{aligned}
{}^2T^C_{2gc} = {}^2E^Q_{gb} &= (-2\sqrt{2}(1\bar{1}-1)+\sqrt{3}(2\bar{0}-1)+3\sqrt{2}(2\bar{1}-2)\\
&- 2\sqrt{2}(\bar{2}1-2)+3\sqrt{2}(10\bar{0})-\sqrt{3}(20-\bar{1})-\sqrt{2}(21-\bar{2})-2\sqrt{2}(1-1-\bar{1})\\
&+ 3\sqrt{2}(0\bar{0}-1)+\sqrt{3}(\bar{1}0-2)-\sqrt{3}(1\bar{0}-2)-3\sqrt{2}(2-\bar{1}-2)\\
&+ 2\sqrt{2}(2-1-\bar{2})+\sqrt{2}(\bar{2}-1-2)+2\sqrt{3}(0-1-\bar{2})-\sqrt{3}(0-\bar{1}-2)-3\sqrt{2}(1-2-\bar{2})\\
&- \sqrt{3}(\bar{0}-1-2)-3\sqrt{2}(2\bar{2}-1)-2\sqrt{3}(\bar{2}10)+\sqrt{3}(21\bar{0})+\sqrt{3}(2\bar{1}0))/4\sqrt{12}
\end{aligned}
$$

${}^2G$

$$
\begin{aligned}
{}^2A^C_{1g} = {}^2A^Q_{1g} &= (\sqrt{2}(10-\bar{1})+\sqrt{3}(2-1-\bar{1})+\sqrt{2}(20-\bar{2})-\sqrt{2}(\bar{1}0-1)\\
&+ \sqrt{3}(1\bar{1}-2)-\sqrt{2}(\bar{2}0-1)+\sqrt{2}(2\bar{2}0)+\sqrt{3}(21\bar{1})+\sqrt{3}(-1-\bar{1}-2)\\
&+ \sqrt{2}(0-2-\bar{2}))/2\sqrt{6}
\end{aligned}
$$

$$
\begin{aligned}
{}^2E^C_{ga} = {}^2A^Q_{1g} &= (10(10-\bar{1})+5\sqrt{6}(2-1-\bar{1})+10(20-\bar{2})-10(\bar{1}0-1)\\
&+ 5\sqrt{6}(1\bar{1}-2)-10(\bar{2}0-2)-14(2\bar{2}0)-7\sqrt{6}(21\bar{1})-7\sqrt{6}(-1-\bar{1}-2)\\
&- 14(0-2-\bar{2}))/4\sqrt{105}
\end{aligned}
$$

$$
\begin{aligned}
{}^2E^C_{gb} = {}^2B^Q_{1g} &= (-4\sqrt{3}(20\bar{0})-3\sqrt{3}(21-\bar{1})-\sqrt{2}(1\bar{1}0)\\
&+ 4\sqrt{3}(\bar{2}1-1)-\sqrt{3}(2\bar{1}-1)-2\sqrt{3}(2\bar{2}-2)-\sqrt{2}(0-1-\bar{1})+\sqrt{3}(1-\bar{1}-2)\\
&- 4\sqrt{3}(1-1-\bar{2})-2\sqrt{3}(2-2-\bar{2})-4\sqrt{3}(0\bar{0}-2)+3\sqrt{3}(\bar{1}-1-2))/2\sqrt{70}
\end{aligned}
$$

$$
\begin{aligned}
{}^2T^C_{1ga} = {}^2A^Q_{2g} &= i(\sqrt{3}(-1-\bar{1}-2)+\sqrt{2}(0-2-\bar{2})-\sqrt{2}(2\bar{2}0)\\
&- \sqrt{3}(21\bar{1}))/\sqrt{10}
\end{aligned}
$$

$$
\begin{aligned}
{}^2T^C_{1gb} = {}^2E^Q_{ga} &= (2\sqrt{6}(1-1-\bar{1})+4(10-\bar{2})-\sqrt{6}(2-\bar{1}-2)\\
&+ 2\sqrt{6}(2-1-\bar{2})+\sqrt{6}(0\bar{0}-1)-7(\bar{1}0-2)+3(1\bar{0}-2)-\sqrt{6}(\bar{2}-1-2)\\
&- \sqrt{6}(10\bar{0})+3(2\bar{0}-1)-7(20-\bar{1})-\sqrt{6}(21-\bar{2})-2\sqrt{6}(1\bar{1}-1)\\
&+ 4(\bar{2}0-1)+2\sqrt{6}(\bar{2}1-2)-\sqrt{6}(2\bar{1}-2)+3(21\bar{0})-2(\bar{2}10)
\end{aligned}
$$

TABLE 17--Continued

$-\ (2\bar{1}0)+\sqrt{6}(2\bar{2}-1)-(0-\bar{1}-2)-2(0-1-\bar{2})-\sqrt{6}(1-2-\bar{2})$
$+\ 3(\bar{0}-1-2))/8\sqrt{5}$

$^2T^C_{1gc} = {}^2E^Q_{gb} = i(2\sqrt{6}(1-1-\bar{1})+4(10-\bar{2})-\sqrt{6}(2-\bar{1}-2)$
$+\ 2\sqrt{6}(2-1-\bar{2})+\sqrt{6}(0\bar{0}-1)-7(\bar{1}0-2)+3(1\bar{0}-2)-\sqrt{6}(\bar{2}-1-2)$
$+\ 6(10\bar{0})-3(2\bar{0}-1)+7(20-\bar{1})+\sqrt{6}(21-\bar{2})+2\sqrt{6}(1\bar{1}-1)$
$-\ 4(\bar{2}0-1)-2\sqrt{6}(\bar{2}1-2)+\sqrt{6}(2\bar{1}-2)+3(21\bar{0})-2(\bar{2}10)-(2\bar{1}0)$
$+\ \sqrt{6}(2\bar{2}-1)+(0-\bar{1}-2)+2(0-1-\bar{2})+\sqrt{6}(1-2-\bar{2})-3(\bar{0}-1-2))/8\sqrt{5}$

$^2T^C_{2ga} = {}^2B^Q_{2g} = i(\sqrt{2}(0-1-\bar{1})-\sqrt{3}(1-\bar{1}-2)+4\sqrt{3}(1-1-\bar{2})$
$+\ 2\sqrt{3}(2-2-\bar{2})+4\sqrt{3}(0\bar{0}-2)-3\sqrt{3}(\bar{1}-1-2)-4\sqrt{3}(20\bar{0})$
$-\ 3\sqrt{3}(21-\bar{1})-\sqrt{2}(1\bar{1}0)+4\sqrt{3}(\bar{2}1-1)-\sqrt{3}(2\bar{1}-1)-2\sqrt{3}(2\bar{2}-2))/2\sqrt{70}$

$^2T^C_{2gb} = {}^2E^Q_{ga} = (\sqrt{6}(10\bar{0})-3(2\bar{0}-1)+7(20-\bar{1})+\sqrt{6}(21-\bar{2})$
$+\ 2\sqrt{6}(1\bar{1}-1)-4(\bar{2}0-1)-2\sqrt{6}(\bar{2}1-2)+\sqrt{6}(2\bar{1}-2)-2\sqrt{6}(1-1-\bar{1})$
$-\ 4(10-\bar{2})+\sqrt{6}(2-\bar{1}-2)-2\sqrt{6}(2-1-\bar{2})-\sqrt{6}(0\bar{0}-1)+7(\bar{1}0-2)$
$-\ 3(1\bar{0}-2)+\sqrt{6}(\bar{2}-1-2)+21(21\bar{0})-14(\bar{2}10)-7(2\bar{1}0)+7\sqrt{6}(2\bar{2}-1)$
$-\ 7(0-\bar{1}-2)-14(0-1-\bar{2})-7\sqrt{6}(1-2-\bar{2})+21(\bar{0}-1-2))/8\sqrt{35}$

$^2T^C_{2gc} = {}^2E^Q_{gb} = i(\sqrt{6}(10\bar{0})-3(2\bar{0}-1)+7(20-\bar{1})+\sqrt{6}(21-\bar{2})$
$+\ 2\sqrt{6}(1\bar{1}-1)-4(\bar{2}0-1)-2\sqrt{6}(\bar{2}1-2)+\sqrt{6}(2\bar{1}-2)+2\sqrt{6}(1-1-\bar{1})+4(10-\bar{2})$
$-\ \sqrt{6}(2-\bar{1}-2)+2\sqrt{6}(2-1-\bar{2})+\sqrt{6}(0\bar{0}-1)-7(\bar{1}0-2)+3(1\bar{0}-2)$
$-\ \sqrt{6}(\bar{2}-1-2)-21(21\bar{0})+14(\bar{2}10)+7(2\bar{1}0)-7\sqrt{6}(2\bar{2}-1)$
$-\ 7(0-\bar{1}-2)-14(0-1-\bar{2})-7\sqrt{6}(1-2-\bar{2})+21(\bar{0}-1-2))/8\sqrt{35}$

TABLE 17--Continued

---

^{2}H

$$
\begin{aligned}
{}^{2}E^{C}_{ga} = {}^{2}A^{Q}_{1g} &= -i(\sqrt{3}(2\bar{2}0)-\sqrt{2}(21\bar{1})+\sqrt{3}(0\text{-}2\text{-}\bar{2}) \\
&- \sqrt{2}(-1\text{-}\bar{1}\text{-}2))/\sqrt{10}
\end{aligned}
$$

$$
\begin{aligned}
{}^{2}E^{C}_{gb} = {}^{2}B^{Q}_{1g} &= i(\sqrt{6}(1\bar{1}0)-3(20\bar{0})-(21\text{-}\bar{1})+3(2\bar{1}\text{-}1) \\
&- 2(\bar{2}1\text{-}1)+(2\bar{2}\text{-}2)+\sqrt{6}(0\text{-}1\text{-}\bar{1})-3(0\bar{0}\text{-}2)+2(1\text{-}1\text{-}\bar{2}) \\
&- 3(1\text{-}\bar{1}\text{-}2)+(\bar{1}\text{-}1\text{-}2)-(2\text{-}2\text{-}\bar{2}))/\sqrt{60}
\end{aligned}
$$

$$
\begin{aligned}
{}^{2}T^{C}_{1ga}-1={}^{2}A^{Q}_{2g} &= (4(1\bar{0}\text{-}1)-2(\bar{1}0\text{-}1)+\sqrt{6}(1\bar{1}\text{-}2) \\
&-\sqrt{6}(2\text{-}1\text{-}\bar{1})-(20\text{-}\bar{2})+2(2\bar{0}\text{-}2)-(\bar{2}0\text{-}2)-2(10\text{-}\bar{1}))/\sqrt{42}
\end{aligned}
$$

$$
\begin{aligned}
{}^{2}T^{C}_{1gb}-1={}^{2}E^{Q}_{ga} &= i(-21\sqrt{3}(-1\text{-}2\text{-}\bar{2})+21\sqrt{3}(2\bar{2}1) \\
&- 7\sqrt{2}(0\text{-}1\text{-}\bar{2})-7\sqrt{2}(\bar{0}\text{-}1\text{-}2)-7\sqrt{3}(1\text{-}2\text{-}\bar{2})+7\sqrt{3}(2\bar{2}\text{-}1)+14\sqrt{2}(0\text{-}\bar{1}\text{-}2) \\
&- 7\sqrt{2}(21\bar{0})+14\sqrt{2}(2\bar{1}0)-7\sqrt{2}(\bar{2}10)+6\sqrt{3}(0\bar{0}\text{-}1)-8\sqrt{3}(1\text{-}1\text{-}\bar{1}) \\
&+ 9\sqrt{2}(1\bar{0}\text{-}2)-6\sqrt{2}(\bar{1}0\text{-}2)+4\sqrt{3}(2\text{-}\bar{1}\text{-}2)-3\sqrt{3}(2\text{-}1\text{-}\bar{2}) \\
&- 3\sqrt{2}(10\text{-}\bar{2})-\sqrt{3}(\bar{2}\text{-}1\text{-}2)+8\sqrt{3}(1\bar{1}\text{-}1)-6\sqrt{3}(10\bar{0})+9\sqrt{2}(2\bar{0}\text{-}1) \\
&- 6\sqrt{2}(20\text{-}\bar{1})-\sqrt{3}(21\text{-}\bar{2})+4\sqrt{3}(2\bar{1}\text{-}2)-3\sqrt{2}(\bar{2}0\text{-}1) \\
&- 3\sqrt{3}(\bar{2}1\text{-}2))/16\sqrt{21}
\end{aligned}
$$

$$
\begin{aligned}
{}^{2}T^{C}_{1gc}-1={}^{2}E^{Q}_{gb} &= (-21\sqrt{3}(-1\text{-}2\text{-}\bar{2})-21\sqrt{3}(2\bar{2}1)-14\sqrt{2}(0\text{-}\bar{1}\text{-}2) \\
&+ 7\sqrt{2}(0\text{-}1\text{-}\bar{2})+7\sqrt{2}(\bar{0}\text{-}1\text{-}2)+7\sqrt{3}(1\text{-}2\text{-}\bar{2})+7\sqrt{3}(2\bar{2}\text{-}1) \\
&- 7\sqrt{2}(21\bar{0})+14\sqrt{2}(2\bar{1}0)-7\sqrt{2}(\bar{2}10)+6\sqrt{3}(0\bar{0}\text{-}1)-8\sqrt{3}(1\text{-}1\text{-}\bar{1}) \\
&+ 9\sqrt{2}(1\bar{0}\text{-}2)-6\sqrt{2}(\bar{1}0\text{-}2)+4\sqrt{3}(2\text{-}\bar{1}\text{-}2)-3\sqrt{3}(2\text{-}1\text{-}\bar{2})-3\sqrt{2}(10\text{-}\bar{2}) \\
&- \sqrt{3}(\bar{2}\text{-}1\text{-}2)-8\sqrt{3}(1\bar{1}\text{-}1)+6\sqrt{3}(10\bar{0})-9\sqrt{2}(2\bar{0}\text{-}1)+6\sqrt{2}(20\text{-}\bar{1}) \\
&+ \sqrt{3}(21\text{-}\bar{2})-4\sqrt{3}(2\bar{1}\text{-}2)+3\sqrt{2}(\bar{2}0\text{-}1)+3\sqrt{3}(\bar{2}1\text{-}2))/16\sqrt{21}
\end{aligned}
$$

TABLE 17--Continued

$$\begin{aligned}{}^{2}T^{C}_{1ga}-2={}^{2}A^{Q}_{2g} &= (\sqrt{3}(2\bar{2}0)-\sqrt{2}(21\bar{1})-\sqrt{3}(0-2-\bar{2})\\ &+ \sqrt{2}(-1-\bar{1}-2))/\sqrt{10}\end{aligned}$$

$$\begin{aligned}{}^{2}T^{C}_{1gb}-2={}^{2}E^{Q}_{ga} &= i(-5\sqrt{3}(-1-2-\bar{2})+5(2\bar{2}1)-18\sqrt{2}(0-\bar{1}-2)+9\sqrt{2}(0-1-\bar{2})\\ &+ 9\sqrt{2}(\bar{0}-1-2)+9\sqrt{3}(1-2-\bar{2})-9\sqrt{3}(2\bar{2}-1)+9\sqrt{2}(21\bar{0})-18\sqrt{2}(2\bar{1}0)\\ &+ 9\sqrt{2}(\bar{2}10)+6\sqrt{3}(0\bar{0}-1)-8\sqrt{3}(1-1-\bar{1})+9\sqrt{2}(1\bar{0}-2)-6\sqrt{2}(\bar{1}0-2)\\ &+ 4\sqrt{3}(2-\bar{1}-2)-3\sqrt{3}(2-1-\bar{2})-3\sqrt{2}(10-\bar{2})-\sqrt{3}(\bar{2}-1-2)+8\sqrt{3}(1\bar{1}-1)\\ &- 6\sqrt{3}(10\bar{0})+9\sqrt{2}(2\bar{0}-1)-6\sqrt{2}(20-\bar{1})-\sqrt{3}(21-\bar{2})+4\sqrt{3}(2\bar{1}-2)\\ &- 3\sqrt{2}(\bar{2}0-1)-3\sqrt{3}(\bar{2}1-2))/16\sqrt{15}\end{aligned}$$

$$\begin{aligned}{}^{2}T^{C}_{1gc}-2={}^{2}E^{Q}_{gb} &= (-5\sqrt{3}(-1-2-\bar{2})-5\sqrt{3}(2\bar{2}1)+18\sqrt{2}(0-\bar{1}-2)\\ &- 9\sqrt{2}(0-1-\bar{2})-9\sqrt{2}(\bar{0}-1-2)-9\sqrt{3}(1-2-\bar{2})-9\sqrt{3}(2\bar{2}-1)+9\sqrt{2}(21\bar{0})\\ &- 18\sqrt{2}(2\bar{1}0)+9\sqrt{2}(\bar{2}10)+6\sqrt{3}(0\bar{0}-1)-8\sqrt{3}(1-1-\bar{1})+9\sqrt{2}(1\bar{0}-2)\\ &- 6\sqrt{2}(\bar{1}0-2)+4\sqrt{3}(2-\bar{1}-2)-3\sqrt{3}(2-1-\bar{2})-3\sqrt{2}(10-\bar{2})-\sqrt{3}(\bar{2}-1-2)\\ &- 8\sqrt{3}(1\bar{1}-1)+6\sqrt{3}(10\bar{0})-9\sqrt{2}(2\bar{0}-1)+6\sqrt{2}(20-\bar{1})+\sqrt{3}(21-\bar{2})\\ &- 4\sqrt{3}(2\bar{1}-2)+3\sqrt{2}(\bar{2}0-1)+3\sqrt{3}(\bar{2}1-2))/16\sqrt{15}\end{aligned}$$

$$\begin{aligned}{}^{2}T^{C}_{2ga}={}^{2}B^{Q}_{2g} &= (\sqrt{6}(1\bar{1}0)-3(20\bar{0})-(21-\bar{1})+3(2\bar{1}-1)-2(\bar{2}1-1)\\ &+ (2\bar{2}-2)-\sqrt{6}(0-1-\bar{1})+3(0\bar{0}-2)-2(1-1-\bar{2})+3(1-\bar{1}-2)-(\bar{1}-1-2)\\ &- (2-2-\bar{2}))/\sqrt{60}\end{aligned}$$

$$\begin{aligned}{}^{2}T^{C}_{2gb} = {}^{2}E^{Q}_{ga} &= -i(30(-1-2-\bar{2})-30(2\bar{2}1)+4\sqrt{6}(0-\bar{1}-2)\\ &- 2\sqrt{6}(0-1-\bar{2})-2\sqrt{6}(\bar{0}-1-2)-6(1-2-\bar{2})+6(2\bar{2}1)-2\sqrt{6}(21\bar{0})\\ &+ 4\sqrt{6}(2\bar{1}0)-2\sqrt{6}(\bar{2}10)+12(0\bar{0}-1)-16(1-1-\bar{1})+6\sqrt{6}(1\bar{0}-2)\\ &- 4\sqrt{6}(\bar{1}0-2)+8(2-\bar{1}-2)-6(2-1-\bar{2})-2\sqrt{6}(10-\bar{2})-2(\bar{2}-1-2)\\ &+ 16(1\bar{1}-1)-12(10\bar{0})+6\sqrt{6}(2\bar{0}-1)-4\sqrt{6}(20-\bar{1})-2(21-\bar{2})+8(2\bar{1}-2)\\ &- 2\sqrt{6}(\bar{2}0-1)-6(\bar{2}1-2))/16\sqrt{15}\end{aligned}$$

TABLE 17--Continued

$$\begin{aligned} {}^2T^C_{2gc} = {}^2E^Q_{gb} &= (-30(-1-2-\bar{2})-30(2\bar{2}1)+4\sqrt{6}(0-\bar{1}-2)-2\sqrt{6}(0-1-\bar{2}) \\ &- 2\sqrt{6}(\bar{0}-1-2)-6(1-2-\bar{2})-6(2\bar{2}-1)+2\sqrt{6}(21\bar{0})-4\sqrt{6}(2\bar{1}0)+2\sqrt{6}(\bar{2}10) \\ &- 12(0\bar{0}-1)+16(1-1-\bar{1})-6\sqrt{6}(1\bar{0}-2)+4\sqrt{6}(\bar{1}0-2)-8(2-\bar{1}-2)+6(2-1-\bar{2}) \\ &+ 2\sqrt{6}(10-\bar{2})+2(\bar{2}-1-2)+16(1\bar{1}-1)-12(10\bar{0})+6\sqrt{6}(2\bar{0}-1)-4\sqrt{6}(20-\bar{1}) \\ &- 2(21-\bar{2})+8(2\bar{1}-2)-2\sqrt{6}(\bar{2}0-1)-6(\bar{2}1-2))/16\sqrt{15} \end{aligned}$$

---

^4P

$$ {}^4T^C_{1ga} = {}^4A^Q_{2g} = (2(10-1)-(20-1))/\sqrt{5} $$

$$\begin{aligned} {}^4T^C_{1gb} = {}^4E^Q_{ga} &= i(\sqrt{2}(10-2)-\sqrt{3}(2-1-2)+\sqrt{2}(20-1) \\ &- \sqrt{3}(21-2))/\sqrt{10} \end{aligned}$$

$$ {}^4T^C_{1gc} = {}^4E^Q_{gb} = (\sqrt{2}(10-2)-\sqrt{3}(2-1-2)-\sqrt{2}(20-1)+\sqrt{3}(21-2))/\sqrt{10} $$

---

^4F

$$ {}^4A^C_{2g} = {}^4B^Q_{1g} = i((1-1-2)-(21-1)/\sqrt{2} $$

$$ {}^4T^C_{1ga} = {}^4A^Q_{2g} = ((10-1)+2(20-2))/\sqrt{5} $$

$$\begin{aligned} {}^4T^C_{1gb} = {}^4E^Q_{ga} &= -i(3(20-1)+\sqrt{6}(21-2)+3(10-2)+\sqrt{6}(2-1-2) \\ &+ 5(0-1-2)+5(210))/4\sqrt{5} \end{aligned}$$

$$\begin{aligned} {}^4T^C_{1gc} = {}^4E^Q_{gb} &= (3(20-1)+\sqrt{6}(21-2)-3(10-2)-\sqrt{6}(2-1-2) \\ &+ 5(0-1-2)-5(210))/4\sqrt{5} \end{aligned}$$

The cubic ligand field potential

The cubic potential, $V_c \equiv V_{O_h}$, and the added axial potential, V_a, that constitute the quadrate field arise due to the coulombic interactions between the central ion's d electrons and the charged ligands. Thus, the general form of the ligand field potential is given by (3).

In this coupling scheme, $\{L,S,\chi^C,\chi^Q,\Gamma^Q\}$, we treat V_c and V_a as individual perturbations. Let us first consider the form of the ligand field potential for an octahedral arrangement of the ligands. As always, the ligands are assumed to be fixed in space at equal distances, a, along the three cartesian axis. The charge of the octahedral ligands is taken as $-q_k$. Utilizing the expansion of $1/r_{ik}$ we have

$$V_c = \sum_k q_k e[\sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{+\ell} \cdot \frac{4\pi}{(2\ell+1)}(\frac{r_<^{\ell}}{r_>^{\ell+1}}) \cdot Y_\ell^{m_\ell}(\theta_i,\phi_i)Y_\ell^{m_\ell *}(\theta_k,\phi_k)] \tag{37}$$

If we consider the electron to be somewhere between the central ion and the ligand (cf. Fig. 5), then $r_<$ is equal to r_i, the distance between the central ion and the electron, and $r_>$ is equal to a, the central ion-ligand separation.

In Fig. 6 we have numbered the ligands and show their locations along the cartesian axis.

Because the ligands are taken as fixed in space, the angles θ_k and ϕ_k are constant for each ligand. Therefore, we can calculate

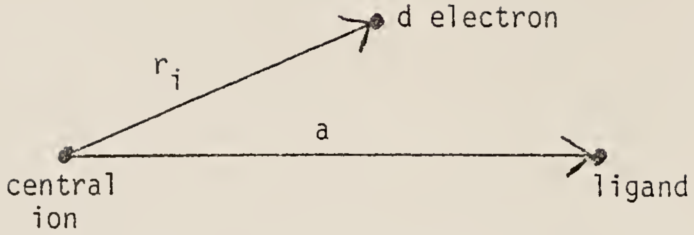

Figure 5. Position of a d Electron in a Complex

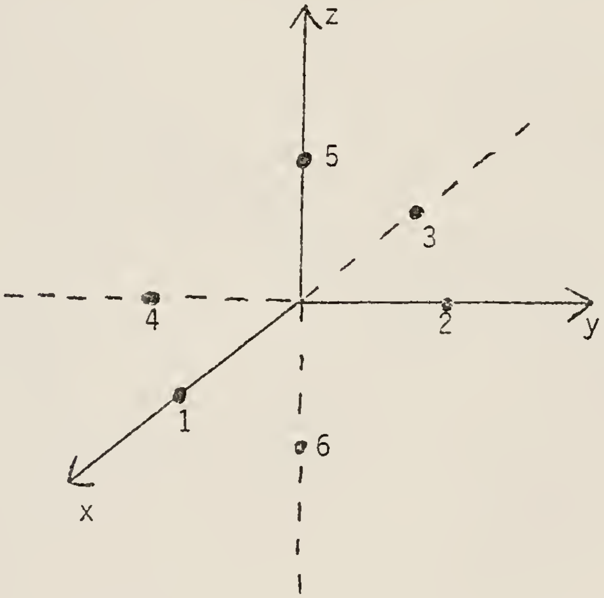

Figure 6. The Numbering of the Ligands for an Octahedral Complex

the spherical harmonics for the ligands, i.e., $Y_{\ell}^{m_\ell}(\theta_k,\phi_k)$. The octahedral potential is thus given by

$$V_{O_h} = \sum_k q_k e\left[\sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{+\ell} D_k Y_{\ell}^{m_\ell}(\theta_i,\phi_i)\right] \tag{38}$$

where

$$D_k = \frac{4\pi}{(2\ell+1)}\left(\frac{r_i^{\ell}}{a^{\ell+1}}\right) Y_{\ell}^{m_\ell *}(\theta_k,\phi_k) \tag{39}$$

with

$$Y_{\ell}^{m_\ell}(\theta_k,\phi_k) = \left[\frac{(2\ell+1)}{2}\cdot\frac{(\ell-|m_\ell|)!}{(\ell+|m_\ell|)!}\right]^{1/2} P_{\ell}^{m_\ell}(\cos\theta)\sqrt{1/2\pi}\; e^{im_\ell\phi} . \tag{40}$$

The Legendre polynomials have the form

$$P_{\ell}^{m_\ell}(\cos\theta) \equiv P_{\ell}^{m_\ell}(z) = (1-z^2)^{\frac{|m_\ell|}{2}} \frac{d^{|m_\ell|}}{dz^{|m_\ell|}} P_{\ell}^{0}(z) \quad \text{and} \tag{41a}$$

$$P_{\ell}^{0}(z) = \frac{1}{2^{\ell}\cdot\ell!}\cdot\frac{d^{\ell}}{dz^{\ell}}(z^2-1)^{\ell} . \tag{41b}$$

For both cubic and tetragonal symmetries the potential must be the same at the points $p(\phi)$ and $p(\phi+\pi/2)$. We know that the ϕ dependent part of the spherical harmonics is given by

$$\Phi(\phi) = \sqrt{1/2\pi}\cdot e^{im_\ell\phi} . \tag{42}$$

Therefore,

$$e^{im_\ell\phi} = e^{im_\ell(\phi+\pi/2)} = e^{im_\ell\phi}\cdot e^{im_\ell(\pi/2)}$$

$$1 = e^{im_\ell(\pi/2)} \quad \text{and}$$

$$1 = \cos\left(\frac{m_\ell\pi}{2}\right) + i\,\sin\left(\frac{m_\ell\pi}{2}\right) \quad . \tag{43}$$

To satisfy (43) m_ℓ is restricted to values of 0, ±4, ±8, etc.

The product of the spherical harmonics for two d electrons, i.e., the spherical harmonics with $\ell = 2$, when written as a sum of spherical harmonics can contain only terms with $\ell = 0$, 2 and 4.

Thus, in the expansion of the ligand field potential, (38), we need only consider those spherical harmonics with ℓ equal to 0, 2 and 4 and m_ℓ equal to 0 and ±4.

Since, as we have noted, the ligands are fixed in space we can calculate D_k using the constant values of the polar angles θ_k and ϕ_k and the sine and cosine of the two polar angles for the six cubic ligands as given in Table 18. Hence, the final form of the potential will contain only those spherical harmonics of the electron for which D_k is not zero. Evaluating (38) we obtain for the octahedral potential

$$V_{O_h} = \sum_i q_k e\sqrt{\pi}[(12/a)Y_0^0 + (7r_i^4/3a^5)Y_4^0 + (\sqrt{70}r_i^4/6a^5)(Y_4^4+Y_4^{-4})] \tag{44}$$

TABLE 18

The θ And ϕ Values For The Ligands Arranged in an Octahedron

Ligand	θ	ϕ	$\sin\theta$	$\cos\theta$	$\sin\phi$	$\cos\phi$
1	$\pi/2$	0	1	0	0	1
2	$\pi/2$	$\pi/2$	1	0	1	0
3	$\pi/2$	π	1	0	0	-1
4	$\pi/2$	$3\pi/2$	1	0	-1	0
5	0	0	0	1	0	1
6	π	0	0	-1	0	1

The Y_0^0 term is a constant, i.e., $Y_0^0 = \sqrt{4\pi}$. This Y_0^0 term in the potential, though of great importance in calculating thermodynamic quantities,[1] can be neglected in deriving the spectral transition energies since it makes a constant contribution to all the levels. Thus, the final form of our cubic potential is

$$V_{O_h} = \sum_i q_k e\sqrt{\pi}(r_i^4/a^5)[(7/3)Y_4^0 + (\sqrt{70}/6)(Y_4^4 + Y_4^{-4})] \ . \qquad (45)$$

The wave functions are linear combinations of the microstates. The microstates are product functions of the single electron orbitals that obey the Pauli principle and are Slater determinants written in shorthand notation as $\psi_1(1)\psi_2(2)\psi_3(3)$ for d^3 electronic configuration. The cubic potential is summed over electrons one, two and three. That is

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[1] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

$$V_{O_h} = V_{O_h}(1) + V_{O_h}(2) + V_{O_h}(3) \quad . \qquad (46)$$

Therefore, the general form of the integrals with which we need concern ourselves here is

$$\int_1 \int_2 \int_3 \psi_1(1)\psi_2(2)\psi_3(3)|V_{O_h}(1) + V_{O_h}(2) + V_{O_h}(3)| \cdot$$

$$\psi_4(1)\psi_5(2)\psi_6(3)d\tau_2 d\tau_2 d\tau_3 \; . \qquad (47a)$$

This becomes

$$\int_1 \psi_1(1)|V_{O_h}(1)|\psi_4(1)d\tau_1 \int_2 \psi_2(2)\psi_5(2)d\tau_2 \;\; \cdot$$

$$\int_3 \psi_3(3)\psi_6(3)d\tau_3 + \int_2 \psi_2(2)|V_{O_h}(2)|\psi_5(2)d\tau_2 \;\; \cdot$$

$$\int_1 \psi_1(1)\psi_4(1)d\tau_1 \int_3 \psi_3(3)\psi_6(3)d\tau_3 +$$

$$\int_3 \psi_3(3)|V_{O_h}(3)|\psi_6(3)d\tau_3 \;\; \int_1 \psi_1(1)\psi_4(1)d\tau_1 \int_2 \psi_2(2)\psi_5(2)d\tau_2 \; . \qquad (47b)$$

Due to the orthonormality of the single electron functions we see that (47) will be zero unless $\psi_2 = \psi_5$ and $\psi_3 = \psi_6$ and/or $\psi_1 = \psi_4$ and $\psi_3 = \psi_6$ and/or $\psi_1 = \psi_4$ and $\psi_2 = \psi_5$.

Thus, the matrix elements reduce to single electron integrals. Since the radial part, which we call R_{3d}, and ℓ, which is equal to 2 for the d-electrons, are constant for the microstates these integrals will be distinguishable only by the different m_ℓ values. Therefore, the single d electron integrals we must calculate are $\langle\pm2|V_{O_h}|\pm2\rangle$, $\langle\pm2|V_{O_h}|\pm1\rangle$, $\langle\pm2|V_{O_h}|0\rangle$, $\langle\pm2|V_{O_h}|\mp1\rangle$, $\langle\pm2|V_{O_h}|\mp2\rangle$, $\langle\pm1|V_{O_h}|\pm1\rangle$, $\langle\pm1|V_{O_h}|0\rangle$, $\langle\pm1|V_{O_h}|\mp1\rangle$ and $\langle0|V_{O_h}|0\rangle$.

Only the spherical harmonics products $Y_2^{\pm2^*}Y_2^{\pm2}$, $Y_2^{\pm1^*}Y_2^{\pm1}$, $Y_2^{0^*}Y_2^{0}$ and $Y_2^{\pm2^*}Y_2^{\mp2}$ contain Y_4^0 or $Y_4^{\pm4}$ (cf. Table 7), which are the spherical harmonics present in the cubic potential (45). Therefore, only the integrals containing these products can be non-zero. These integrals are $\langle\pm2|V_{O_h}|\pm2\rangle$, $\langle\pm1|V_{O_h}|\pm1\rangle$, $\langle0|V_{O_h}|0\rangle$ and $\langle\pm2|V_{O_h}|\mp2\rangle$.

As an illustration of the method of 'solving' the four remaining integrals let us take as an example $\langle2|V_{O_h}|2\rangle$. Thus,

$$\langle2|V_{O_h}|2\rangle = \int R_{3d}^{\ *}Y_2^{2^*}\,|V_{O_h}|\,R_{3d}Y_2^{2}d\tau \ . \qquad (48a)$$

From Table 7 we obtain, neglecting the constant Y_0^0 term,

$$Y_2^{2^*}Y_2^{2} = Y_4^{0^*}/14\sqrt{\pi} - \sqrt{5}Y_2^{0^*}/7\sqrt{\pi} \ .$$

Expanding (48a) we obtain

$$\langle2|V_{O_h}|2\rangle = \int_0^\infty R_{3d}^{\ *}R_{3d}(q_k e)\left(\frac{r_i^{\ 4}}{a^5}\right) \ \cdot$$

$$r^2dr \int_0^{2\pi}\int_0^{\pi} [Y_4^{0*}/14\sqrt{\pi} - \sqrt{5}\, Y_2^{0*}/7\sqrt{\pi}] \cdot$$

$$[7\sqrt{\pi}\, Y_4^0/3 + \sqrt{70\pi}(Y_4^4+Y_4^{-4})/6]\sin\theta d\theta d\phi \ . \tag{48b}$$

Because of the orthonormality of the spherical harmonics (48b) reduces to

$$<2|V_{O_h}|2> = (q_k e/6a^5) \int_0^{\infty} R_{3d}^{*} R_{3d}(r_i^4) r^2 dr \tag{48c}$$

$$<2|V_{O_h}|2> = (q_k e/6a^5)<r_i^4> \ . \tag{48d}$$

As is the usual procedure in ligand field calculations, we will make no effort to solve for the average value of r_i^4. Rather, we define the single electron matrix element to be the well-known cubic parameter Dq, that is,

$$Dq \equiv <2|V_{O_h}|2> = (q_k e/6a^5)<r_i^4> \ . \tag{49}$$

Because the octahedral potential contains only fourth order harmonics, i.e., $\ell = 4$, we need only one parameter, Dq, for the cubic case.

The other non-zero integrals are calculated in the same fashion and they are given below.

$$<\pm 2|V_{O_h}|\pm 2> = Dq \tag{50a}$$

$$\langle \pm 1 | V_{O_h} | \pm 1 \rangle = -4Dq \tag{50b}$$

$$\langle 0 | V_{O_h} | 0 \rangle = 6Dq \tag{50c}$$

$$\langle \pm 2 | V_{O_h} | \mp 2 \rangle = 5Dq \tag{50d}$$

Using the single electron integrals tabulated above we can easily find the values of the d^3 matrix elements in terms of the cubic field parameter Dq. The energy matrices thus obtained from the block diagonalized secular determinant, (cf. Fig. 4) are listed in Table 19.

The Axial Ligand Field

In order to describe the tetragonal potential as the sum of a cubic and an axial field we must define the charge on the axial ligands, which we will call q', to be

$$q' = q_a - q_e \tag{51}$$

where q_a is the charge on the two axial ligands and q_e is the charge on the four equatorial ligands of the tetragonal complex, (cf. Fig. 1).

The form of the axial potential is analogous to that of the cubic potential and is given by

$$V_a = \sum_k q'e\left[\sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{+\ell} \cdot D_k \cdot Y_\ell^{m_\ell}(\theta_i,\phi_i)\right] . \tag{52}$$

For d electrons, as we have noted, only those terms in the summation

TABLE 19

The Elements of the Cubic Energy Matrices (the H'_{jk}'s) for d^3 Electronic Configuration in the $\{L,S,X^C,X^Q,\Gamma^Q\}$ Coupling Scheme

	$^2A^C_{1g}$	
j	k	H'_{jk}
^2G	^2G	$-11B+3C-2Dq$
	$^2A^C_{2g}$	
^2F	^2F	$9B+3C-2Dq$

			$^2E^C_g$		
j	k	H'_{jk}	j	k	H'_{jk}
^2D-a	^2D-a	$7B+7C+3Dq$	^2D-b	^2G	$24\sqrt{5}Dq/7$
^2D-a	^2D-b	$3\sqrt{21}B-15Dq/\sqrt{21}$	^2D-b	^2H	$i10Dq/\sqrt{70}$
^2D-a	^2G	$-60Dq/\sqrt{105}$	^2G	^2G	$-11B+3C-2Dq/7$
^2D-a	^2H	$-i\sqrt{30}Dq$	^2G	^2H	$i36Dq/\sqrt{14}$
^2D-b	^2D-b	$3B+3C-19Dq/7$	^2H	^2H	$-6B+3C+2Dq$
			$^2T^C_{1g}$		
^2P	^2P	$-6B+3C$	^2P	^2G	$i18Dq/\sqrt{42}$
^2P	^2F	$22Dq/\sqrt{14}$	^2P	$-1(^2H)$	$2\sqrt{5}Dq$

TABLE 19--Continued

j	k	H'_{jk}	j	k	H'_{jk}
^2P	$-2(^2H)$	$6Dq/\sqrt{7}$	^2G	$-1(^2H)$	$i\sqrt{210}Dq/7$
^2F	^2F	$9B+3C+Dq$	^2G	$-2(^2H)$	$i3\sqrt{6}Dq$
^2F	^2G	$-i\sqrt{3}Dq$	$-1(^2H)$	$-1(^2H)$	$-6B+3C-2Dq$
^2F	$-1(^2H)$	$10Dq/\sqrt{70}$	$-1(^2H)$	$-2(^2H)$	$-2\sqrt{35}Dq/7$
^2F	$-2(^2H)$	$-\sqrt{2}Dq$	$-2(^2H)$	$-2(^2H)$	$-6B+3C+2Dq$
^2G	^2G	$-11B+3C-Dq$			
			$^2T^C_{2g}$		
$^2D\text{-}a$	$^2D\text{-}a$	$7B+7C-2Dq$	$^2D\text{-}b$	^2H	$i40Dq/3\sqrt{70}$
$^2D\text{-}a$	$^2D\text{-}b$	$3\sqrt{21}B+10Dq/\sqrt{21}$	^2F	^2F	$9B+3C-Dq/3$
$^2D\text{-}a$	^2F	$-i10Dq/\sqrt{3}$	^2F	^2G	$-i15Dq/\sqrt{35}$
$^2D\text{-}a$	^2G	$30Dq/\sqrt{105}$	^2F	^2H	$-\sqrt{10}Dq/3$
$^2D\text{-}a$	^2H	$-i40Dq/\sqrt{30}$	^2G	^2G	$-11B+3C+13Dq/7$
$^2D\text{-}b$	$^2D\text{-}b$	$3B+3C+38Dq/21$	^2G	^2H	$-i6Dq/\sqrt{14}$
$^2D\text{-}b$	^2F	$-i20Dq/3\sqrt{7}$	^2H	^2H	$-6B+3C-4Dq/3$
$^2D\text{-}b$	^2G	$-12\sqrt{5}Dq/7$			

$^4A^C_{2g}$

j	k	H'_{jk}
^4F	^4F	$-15B-12Dq$

TABLE 19--Continued

	$^4T_{1g}^C$	
j	k	H'_{jk}
^4P	^4P	0
^4P	^4F	-4Dq
^4F	^4F	-15B+6Dq
	$^4T_{2g}^C$	
^4F	^4F	-15B-2Dq

with $\ell = 0$, 2 and 4 need be considered. Also, since for axial symmetry the principal rotation axis is C_∞ the potential must be the same for all values of ϕ. That is, $p(\phi) = p(\phi+\alpha)$ with α taking all real values. Thus,

$$e^{im_\ell \phi} = e^{im_\ell(\phi+\alpha)} \tag{53}$$

which can hold true for all values of α only if $m_\ell = 0$. Hence, the axial potential can be written as

$$V_a = \sum_k q'e[\sum_{\ell \leq 4} D_k' \cdot Y_\ell^0(\theta_i,\phi_i)] \tag{54a}$$

with

$$D_k' = \frac{4\pi}{(2\ell+1)} \left(\frac{r_i^\ell}{a^{\ell+1}} \right) Y_\ell^0(\theta_k,\phi_k) \ . \tag{54b}$$

The axial field potential for the two ligands turns out to be

$$V_a = q'e\sqrt{\pi}[(4/a)Y_0^0 + (4r_i^2/5a^3)Y_2^0 + (4r_i^4/3a^5)Y_4^0] \tag{55a}$$

or, leaving out the constant Y_0^0 term,

$$V_a = q'e\sqrt{\pi}[4r_i^2/5a^3)Y_2^0 + (4r_i^4/3a^5)Y_4^0] \ . \tag{55b}$$

Only the spherical harmonics products $Y_2^{\pm2*}Y_2^{\pm2}$, $Y_2^{\pm1*}Y_2^{\pm1}$ and $Y_2^{0*}Y_2^0$ contain Y_2^0 or Y_4^0, (cf. Table 7), which are the spherical harmonics present in the axial potential (55b). Therefore, only the integrals containing these products can be non-zero. These integrals are $<\pm 2|V_a|\pm 2>$, $<\pm 1|V_a|\pm 1>$ and $<0|V_a|0>$.

As an illustration of the method of 'solving' these three remaining integrals let us take as an example $<2|V_a|2>$. Thus,

$$<2|V_a|2> = \int R_{3d}{}^{*}Y_2{}^{2^*}|V_a|R_{3d}Y_2{}^{2}d\tau. \tag{56a}$$

Expanding (56a) we obtain

$$\begin{aligned} <2|V_a|2> = &\int_0^\infty R_{3d}{}^{*}R_{3d}(q'e)\left(\frac{r_i{}^2}{a^3}\right)r^2dr \cdot \\ &\int_0^{2\pi}\int_0^{\pi}(-\sqrt{5}\,Y_2{}^{0^*}/7\sqrt{\pi})(4\sqrt{\pi}\,Y_2{}^{0}/\sqrt{5})\sin\theta d\theta d\phi \; + \\ &\int_0^\infty R_{3d}{}^{*}R_{3d}(q'e)\left(\frac{r_i{}^4}{a^5}\right)r^2dr \int_0^{2\pi}\int_0^{\pi}(Y_4{}^{0^*}/14\sqrt{\pi}) \cdot \\ &(r\sqrt{\pi}\,Y_4{}^{0}/3)\sin\theta d\theta d\phi \; . \end{aligned} \tag{56b}$$

Because of the orthonormality of the spherical harmonics (56b) reduces to

$$<2|V_a|2> = (-4q'e/7a^3)<r_i{}^2> + (2a'3/21a^5)<r_i{}^4> \quad . \tag{56c}$$

As in the cubic case we will make no effort to solve for the average values of $r_i{}^2$ and $r_i{}^4$. Rather, we define two new parameters, Dt and Ds, as follows

$$Dt = (2q'e/21a^5)\langle r_i^4 \rangle \tag{57a}$$

and

$$Ds = (2q'e/7a^3)\langle r_i^2 \rangle \quad . \tag{57b}$$

Thus, $\langle 2|V_a|2\rangle$ is equal to $-2Ds + Dt$.

These axial parameters, Dt and Ds, are equivalently defined as

$$Dt = \langle \pm 2|V_a^{(4)}|\pm 2\rangle \tag{58a}$$

and

$$Ds = \langle \pm 1|V_a^{(2)}|\pm 1\rangle \quad . \tag{58b}$$

Where for Dt only the fourth order harmonic of the axial potential, i.e., the Y_4^0 term, is used and for Ds only the second order harmonic of the axial potential, i.e., the Y_2^0 term, is used.

The non-zero integrals for the axial perturbation are

$$\langle \pm 2|V_a|\pm 2\rangle = -2Ds + Dt \tag{59a}$$

$$\langle \pm 1|V_a|\pm 1\rangle = Ds - 4Dt \tag{59b}$$

$$\langle 0|V_a|0\rangle = 2Ds + 6Dt \tag{59c}$$

The wave functions used for the axial calculations are obtained simply by the symmetry decomposition of the cubic functions, (cf. Tables 15, 16 and 17).

Here, also, we can block diagonalize the secular determinant due to the fact that only those matrix elements between states that belong to the same tetragonal irreducible representation can be non-zero. This is illustrated in Fig. 7.

The resulting tetragonal energy matrices are listed in Table 20.

To obtain the complete energy matrices for the d^3 weak field case, without the spin-orbit perturbation, one appropriately superimposes the cubic matrices (given in Table 19) onto the tetragonal matrices (given in Table 20).

The Spin-Orbit Interaction[1]

In considering the transformation properties of wave functions we have so far neglected the symmetry properties of the spin part of the wave function. In considering the spin-orbit perturbation we must construct the wave functions so that they transform as the irreducible representations, to which they belong, inclusive of both space and spin.

Equation (26) gives the character of the representation corresponding to a rotation operation for a wave function with angular momentum L. That is,

$$\chi(\alpha) = \frac{\sin[(L+1/2)\alpha]}{\sin(\alpha/2)} \qquad (26)$$

where α is the angle of rotation.

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[1] F. A. Cotton, Chemical Applications of Group Theory, 2nd ed., Wiley-Interscience, New York, 1971.

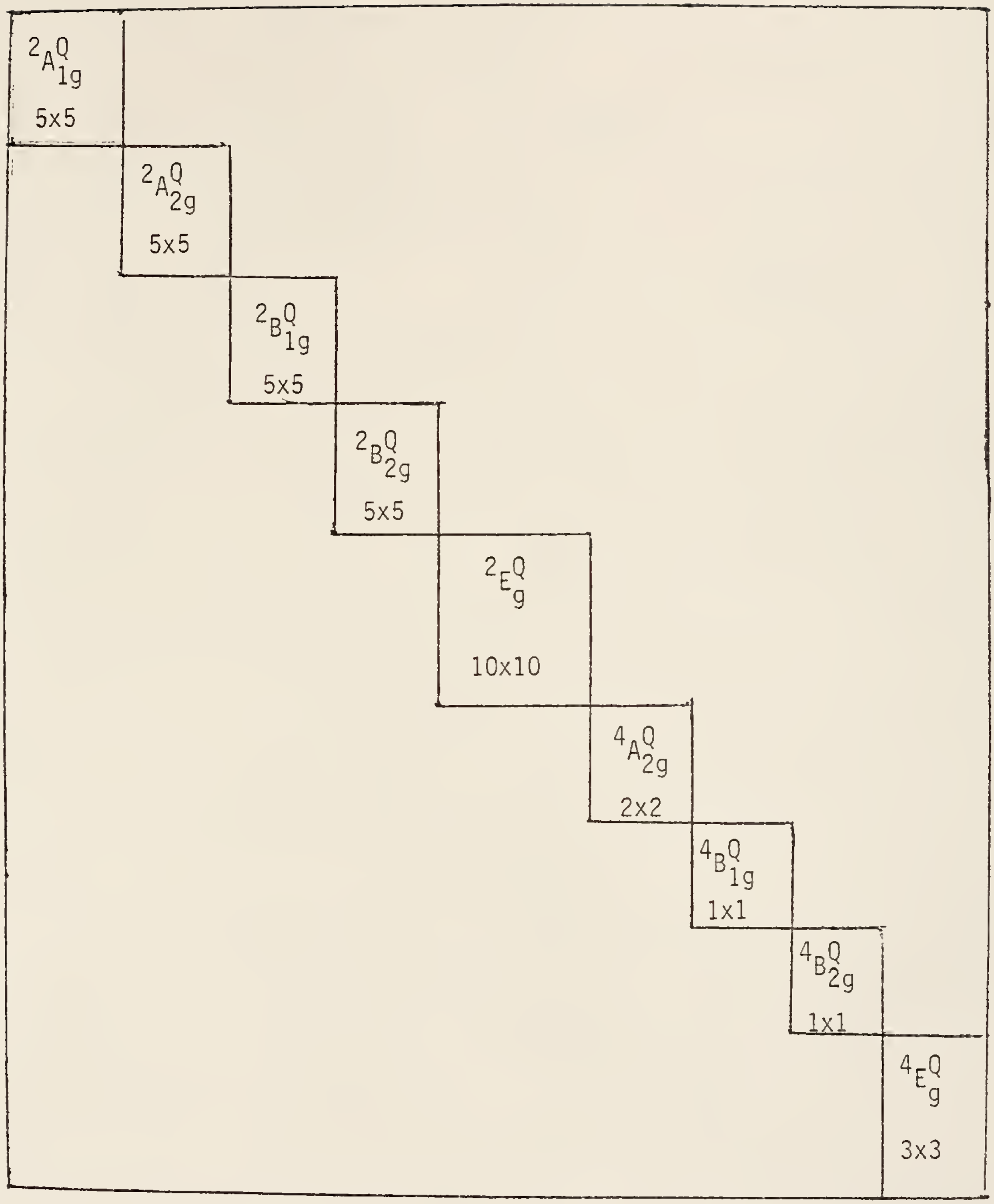

Figure 7. The tetragonal secular determinant for d^3 for the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme.

TABLE 20

The Elements for the Axial Ligand Field
Purturbation of the $\{L,S,X^C,X^Q,\Gamma^Q\}$
Coupling Scheme

	$^2A^Q_{1g}$	
j	k	H'_{jk}
$^2E^C_g(^2D\text{-}a)$	$^2E^C_g(^2D\text{-}a)$	$Ds+3Dt$
$^2E^C_g(^2D\text{-}a)$	$^2E^C_g(^2D\text{-}b)$	$3(3Ds-5Dt)/\sqrt{21}$
$^2E^C_g(^2D\text{-}a)$	$^2A^C_{1g}(^2G)$	$(3Ds-5Dt)/\sqrt{3}$
$^2E_g(^2D\text{-}a)$	$^2E^C_g(^2G)$	$5(3Ds-5Dt)/\sqrt{105}$
$^2E^C_g(^2D\text{-}a)$	$^2E^C_g(^2H)$	0
$^2E^C_g(^2D\text{-}b)$	$^2E^C_g(^2D\text{-}b)$	$(3Ds-19Dt)/7$
$^2E^C_g(^2D\text{-}b)$	$^2A^C_{1g}(^2G)$	$(Ds+10Dt)/\sqrt{7}$
$^2E^C_g(^2D\text{-}b)$	$^2E^C_g(^2G)$	$\sqrt{5}(Ds+10Dt)/7$
$^2E^C_g(^2D\text{-}b)$	$^2E^C_g(^2H)$	0
$^2A^C_{1g}(^2G)$	$^2A^C_{1g}(^2G)$	$-7Dt/6$

TABLE 20--Continued

j	k	H'_{jk}
$^2A^C_{1g}(^2G)$	$^2E^C_g(^2G)$	$(24Ds-5Dt)/6\sqrt{35}$
$^2A^C_{1g}(^2G)$	$^2E^C_g(^2H)$	$i(2Ds-15Dt)/\sqrt{10}$
$^2E^C_g(^2G)$	$^2E^C_g(^2G)$	$-(48Ds+235Dt)/210$
$^2E^C_g(^2G)$	$^2E^C_g(^2H)$	$-i\sqrt{14}(2Ds-15Dt)/10$
$^2E^C_g(^2H)$	$^2E^C_g(^2H)$	$-2(3Ds-5Dt)/5$
	$^2A^Q_{2g}$	
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}(^2P)$	$-4Ds/5$
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}(^2F)$	$-2(12Ds-55Dt)/5\sqrt{14}$
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}(^2G)$	0
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}\text{-}1(^2H)$	$2\sqrt{5}Dt$
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}\text{-}2(^2H)$	0
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}(^2F)$	$(4Ds+5Dt)/5$

TABLE 20--Continued

j	k	H'_{jk}
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}(^2G)$	0
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}\text{-}1(^2H)$	$-10(2Ds-Dt)/\sqrt{70}$
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}\text{-}2(^2H)$	0
$^2T^C_{1g}(^2G)$	$^2T^C_{1g}(^2G)$	$-(4Ds+5Dt)/5$
$^2T^C_{1g}(^2G)$	$^2T^C_{1g}\text{-}1(^2H)$	0
$^2T^C_{1g}(^2G)$	$^2T^C_{1g}\text{-}2(^2H)$	$-i\sqrt{6}(2Ds-15Dt)/5$
$^2T^C_{1g}\text{-}1(^2H)$	$^2T^C_{1g}\text{-}1(^2H)$	$2(Ds-Dt)$
$^2T^C_{1g}\text{-}1(^2H)$	$^2T^C_{1g}\text{-}2(^2H)$	0
$^2T^C_{1g}\text{-}2(^2H)$	$^2T^C_{1g}\text{-}2(^2H)$	$-2(3Ds-5Dt)/5$
	$^2B^Q_{1g}$	
$^2E^C_g(^2D\text{-}a)$	$^2E^C_g(^2D\text{-}a)$	$-(2Ds-Dt)/2$
$^2E^C_g(^2D\text{-}a)$	$^2E^C_g(^2D\text{-}b)$	$-(18Ds+5Dt)/\sqrt{84}$

TABLE 20--Continued

j	k	H'_{jk}
${}^2E_g^C({}^2D\text{-}a)$	${}^2A_{2g}^C({}^2F)$	$-i(3Ds-5Dt)/\sqrt{3}$
${}^2E_g^C({}^2D\text{-}a)$	${}^2E_g^C({}^2G)$	$-15(Ds+3Dt)/\sqrt{105}$
${}^2E_g^C({}^2D\text{-}a)$	${}^2E_g^C({}^2H)$	$-i35Dt/\sqrt{30}$
${}^2E_g^C({}^2D\text{-}b)$	${}^2E_g^C({}^2D\text{-}b)$	$-(18Ds+19Dt)/42$
${}^2E_g^C({}^2D\text{-}b)$	${}^2A_{2g}^C({}^2F)$	$-i(27Ds-1Dt)/3\sqrt{7}$
${}^2E_g^C({}^2D\text{-}b)$	${}^2E_g^C({}^2G)$	$-\sqrt{5}(Ds-18Dt)/7$
${}^2E_g^C({}^2D\text{-}b)$	${}^2E_g^C({}^2H)$	$i\sqrt{70}Dt/6$
${}^2A_{2g}^C({}^2F)$	${}^2A_{2g}^C({}^2F)$	$-7Dt/6$
${}^2A_{2g}^C({}^2F)$	${}^2E_g^C({}^2G)$	$i(16Ds-15Dt)/2\sqrt{35}$
${}^2A_{2g}^C({}^2F)$	${}^2E_g^C({}^2H)$	$(18Ds+5Dt)/\sqrt{90}$
${}^2E_g^C({}^2G)$	${}^2E_g^C({}^2G)$	$(16Ds+55Dt)/70$

TABLE 20--Continued

j	k	H'_{jk}
$^2E_g^C(^2G)$	$^2E_g^C(^2H)$	$i\sqrt{14}(2Ds+15Dt)/10$
$^2E_g^C(^2H)$	$^2E_g^C(^2H)$	$(18Ds+5Dt)/15$
	$^2B_{2g}^Q$	
$^2T_{2g}^C(^2D\text{-}a)$	$^2T_{2g}^C(^2D\text{-}a)$	$-(2Ds-Dt)/2$
$^2T_{2g}^C(^2D\text{-}a)$	$^2T_{2g}^C(^2D\text{-}b)$	$-(18Ds+5Dt)/\sqrt{84}$
$^2T_{2g}^C(^2D\text{-}a)$	$^2T_{2g}^C(^2F)$	$i(3Ds-5Dt)/\sqrt{3}$
$^2T_{2g}^C(^2D\text{-}a)$	$^2T_{2g}^C(^2G)$	$\sqrt{105}(Ds+3Dt)/7$
$^2T_{2g}^C(^2D\text{-}a)$	$^2T_{2g}^C(^2H)$	$-i35Dt/\sqrt{30}$
$^2T_{2g}^C(^2D\text{-}b)$	$^2T_{2g}^C(^2D\text{-}b)$	$-(18Ds+19Dt)/42$
$^2T_{2g}^C(^2D\text{-}b)$	$^2T_{2g}^C(^2F)$	$i(27Ds-10Dt)/3\sqrt{7}$
$^2T_{2g}^C(^2D\text{-}b)$	$^2T_{2g}(^2G)$	$\sqrt{5}(Ds-18Dt)/7$
$^2T_{2g}^C(^2D\text{-}b)$	$^2T_{2g}^C(^2H)$	$i\sqrt{70}Dt/6$

TABLE 20--Continued

j	k	H'_{jk}
$^2T^C_{2g}(^2F)$	$^2T^C_{2g}(^2F)$	$-7Dt/6$
$^2T^C_{2g}(^2F)$	$^2T^C_{2g}(^2G)$	$i(16Ds-15Dt)/2\sqrt{35}$
$^2T^C_{2g}(^2F)$	$^2T^C_{2g}(^2H)$	$-(18Ds+5Dt)/\sqrt{90}$
$^2T^C_{2g}(^2G)$	$^2T^C_{2g}(^2G)$	$(16Ds+55Dt)/70$
$^2T^C_{2g}(^2G)$	$^2T^C_{2g}(^2H)$	$-i\sqrt{14}(2Ds+15Dt)/10$
$^2T^C_{2g}(^2H)$	$^2T^C_{2g}(^2H)$	$(18Ds+5Dt)/15$
	$^2E^Q_g$	
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}(^2P)$	$2Ds/5$
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}(^2F)$	$3(16Ds+55Dt)/20\sqrt{14}$
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}(^2G)$	$i3\sqrt{42}Dt/8$
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}\text{-}1(^2H)$	$3\sqrt{5}Dt/4$
$^2T^C_{1g}(^2P)$	$^2T^C_{1g}\text{-}2(^2H)$	$3\sqrt{7}Dt/4$

TABLE 20--Continued

j	k	H'_{jk}
$^2T^C_{1g}(^2P)$	$^2T^C_{2g}(^2D\text{-}a)$	$-i21Ds/\sqrt{70}$
$^2T^C_{1g}(^2P)$	$^2T^C_{2g}(^2D\text{-}b)$	$i3Ds/\sqrt{30}$
$^2T^C_{1g}(^2P)$	$^2T^C_{2g}(^2F)$	$-3(16Ds+55Dt)/4\sqrt{210}$
$^2T^C_{1g}(^2P)$	$^2T^C_{2g}(^2G)$	$-i9Dt/4\sqrt{6}$
$^2T^C_{1g}(^2P)$	$^2T^C_{2g}(^2H)$	$-\sqrt{21}Dt/2$
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}(^2F)$	$-(16Ds-15Dt)/40$
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}(^2G)$	$-i7\sqrt{3}Dt/8$
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}\text{-}1(^2H)$	$\sqrt{70}(8Ds+3Dt)/56$
$^2T^C_{1g}(^2F)$	$^2T^C_{1g}\text{-}2(^2H)$	$-7\sqrt{2}Dt/8$
$^2T^C_{1g}(^2F)$	$^2T^C_{2g}(^2D\text{-}a)$	$-i(6Ds+25Dt)/4\sqrt{5}$
$^2T^C_{1g}(^2F)$	$^2T^C_{2g}(^2D\text{-}b)$	$-i(27Ds+25Dt)/\sqrt{420}$
$^2T^C_{1g}(^2F)$	$^2T^C_{2g}(^2F)$	$-(24Ds-5Dt)/8\sqrt{15}$

TABLE 20--Continued

j	k	H'_{jk}
$^2T^C_{1g}(^2F)$	$^2T^C_{2g}(^2G)$	$-i\sqrt{21}(16Ds+13Dt)/56$
$^2T^C_{1g}(^2F)$	$^2T^C_{2g}(^2H)$	$-(12Ds+Dt)/4\sqrt{6}$
$^2T^C_{1g}(^2G)$	$^2T^C_{1g}(^2G)$	$(16Ds-15Dt)/40$
$^2T^C_{1g}(^2G)$	$^2T^C_{1g}\text{-}1(^2H)$	$i\sqrt{210}Dt/8$
$^2T^C_{1g}(^2G)$	$^2T^C_{1g}\text{-}2(^2H)$	$i\sqrt{6}(8Ds+45Dt)/40$
$^2T^C_{1g}(^2G)$	$^2T^C_{2g}(^2D\text{-}a)$	$\sqrt{15}(2Ds-Dt)/4$
$^2T^C_{1g}(^2G)$	$^2T^C_{2g}(^2D\text{-}b)$	$\sqrt{35}(Ds+3Dt)/14$
$^2T^C_{1g}(^2G)$	$^2T^C_{2g}(^2F)$	$i(16Ds-15Dt)/8\sqrt{5}$
$^2T^C_{1g}(^2G)$	$^2T^C_{2g}(^2G)$	$-3(8Ds-25Dt)/40\sqrt{7}$
$^2T_{1g}(^2G)$	$^2T^C_{2g}(^2H)$	$-i\sqrt{2}(4Ds+75Dt)/40$
$^2T^C_{1g}\text{-}1(^2H)$	$^2T^C_{1g}\text{-}1(^2H)$	$-(4Ds+3Dt)/4$
$^2T^C_{1g}\text{-}1(^2H)$	$^2T^C_{1g}\text{-}2(^2H)$	$-\sqrt{35}Dt/4$

TABLE 20--Continued

j	k	H'_{jk}
$^2T^C_{1g}-1(^2H)$	$^2T^C_{2g}(^2D-a)$	$-i5\sqrt{14}Dt/8$
$^2T^C_{1g}-1(^2H)$	$^2T^C_{2g}(^2D-b)$	$i5Dt/4\sqrt{6}$
$^2T^C_{1g}-1(^2H)$	$^2T^C_{2g}(^2F)$	$-(3Ds-5Dt)/\sqrt{42}$
$^2T^C_{1g}-1(^2H)$	$^2T^C_{2g}(^2G)$	$i\sqrt{30}(2Ds+5Dt)/20$
$^2T^C_{1g}-1(^2H)$	$^2T^C_{2g}(^2H)$	$-\sqrt{105}(12Ds+5Dt)/60$
$^2T^C_{1g}-2(^2H)$	$^2T^C_{1g}-2(^2H)$	$3(4Ds+5Dt)/20$
$^2T^C_{1g}-2(^2H)$	$^2T_{2g}(^2D-a)$	$-i7\sqrt{10}Dt/8$
$^2T_{1g}-2(^2H)$	$^2T_{2g}(^2D-b)$	$i\sqrt{210}Dt/24$
$^2T^C_{1g}-2(^2H)$	$^2T^C_{2g}(^2F)$	$-(18Ds+5Dt)/2\sqrt{30}$
$^2T^C_{1g}-2(^2H)$	$^2T^C_{2g}(^2G)$	$-i\sqrt{42}Ds/10$
$^2T^C_{1g}-2(^2H)$	$^2T^C_{2g}(^2H)$	$-\sqrt{3}(36Ds-25Dt)/60$
$^2T^C_{2g}(^2D-a)$	$^2T^C_{2g}(^2D-a)$	$(Ds-4Dt)/2$

TABLE 20--Continued

j	k	H'_{jk}
$^2T^C_{2g}(^2D\text{-}a)$	$^2T_{2g}(^2D\text{-}b)$	$(9Ds+20Dt)/\sqrt{84}$
$^2T^C_{2g}(^2D\text{-}a)$	$^2T^C_{2g}(^2F)$	$-i(6Ds+25Dt)/4\sqrt{3}$
$^2T_{2g}(^2D\text{-}a)$	$^2T^C_{2g}(^2G)$	$-\sqrt{105}(2Ds-Dt)/28$
$^2T^C_{2g}(^2D\text{-}a)$	$^2T^C_{2g}(^2H)$	$-i7\sqrt{30}Dt/12$
$^2T^C_{2g}(^2D\text{-}b)$	$^2T^C_{2g}(^2D\text{-}b)$	$(9Ds+76Dt)/42$
$^2T^C_{2g}(^2D\text{-}b)$	$^2T^C_{2g}(^2F)$	$-i(27Ds+25Dt)/6\sqrt{7}$
$^2T^C_{2g}(^2D\text{-}b)$	$^2T^C_{2g}(^2G)$	$-\sqrt{5}(Ds+3Dt)/14$
$^2T^C_{2g}(^2D\text{-}b)$	$^2T^C_{2g}(^2H)$	$i\sqrt{70}Dt/12$
$^2T^C_{2g}(^2F)$	$^2T^C_{2g}(^2F)$	$7Dt/24$
$^2T^C_{2g}(^2F)$	$^2T^C_{2g}(^2G)$	$-i(32Ds+75Dt)/8\sqrt{35}$
$^2T^C_{2g}(^2F)$	$^2T^C_{2g}(^2H)$	$(36Ds-25Dt)/12\sqrt{10}$
$^2T^C_{2g}(^2G)$	$^2T^C_{2g}(^2G)$	$-(32Ds-34Dt)/280$

TABLE 20--Continued

j	k	H'_{jk}
${}^2T^C_{2g}({}^2G)$	${}^2T^C_{2g}({}^2H)$	$i\sqrt{14}(4Ds+15Dt)/40$
${}^2T^C_{2g}({}^2H)$	${}^2T^C_{2g}({}^2H)$	$-(9Ds+20Dt)/15$
	${}^4A^Q_{2g}$	
${}^4T^C_{1g}({}^4P)$	${}^4T^C_{1g}({}^4P)$	$14Ds/5$
${}^4T^C_{1g}({}^4P)$	${}^4T^C_{1g}({}^4F)$	$4(3Ds-5Dt)/5$
${}^4T^C_{1g}({}^4F)$	${}^4T_{1g}({}^4F)$	$-2(2Ds-15Dt)/5$
	${}^4B^Q_{1g}$	
${}^4A^C_{2g}({}^4F)$	${}^4A^C_{2g}({}^4F)$	$-7Dt$
	${}^4B^Q_{2g}$	
${}^4T^C_{2g}({}^4F)$	${}^4T^C_{2g}({}^4F)$	$-7Dt$
	${}^4E^Q_{g}$	
${}^4T^C_{1g}({}^4P)$	${}^4T^C_{1g}({}^4P)$	$-7Ds/5$
${}^4T^C_{1g}({}^4P)$	${}^4T^C_{1g}({}^4F)$	$-3(4Ds+5Dt)/10$

TABLE 20--Continued

j	k	H'_{jk}
$^4T^C_{1g}(^4P)$	$^4T^C_{2g}(^4F)$	$\sqrt{15}(4Ds+5Dt)/10$
$^4T^C_{1g}(^4F)$	$^4T^C_{1g}(^4F)$	$(8Ds+45Dt)/20$
$^4T^C_{1g}(^4F)$	$^4T^C_{2g}(^4F)$	$\sqrt{15}(4Ds+5Dt)/20$
$^4T^C_{2g}(^4F)$	$^4T^C_{2g}(^4F)$	$7Dt/4$

When we include spin we must consider the total angular momentum J which is equal to L + S. If J is an integer then (26) will give the characters of the various representations for each class when we simply interchange L and J. J will be an integer whenever we have an even number of electrons.

For an odd number of electrons (like d^3) J will not be an integer. Let us see what result is obtained when we use (26) to derive the characters when J is not an integer.

For rotation by 2π we expect

$$\chi(\alpha) = \chi(\alpha+2\pi) \ . \tag{60}$$

For simplicity let us consider J = 1/2. Thus

$$\chi(\alpha+2\pi) = \frac{\sin[(1/2+1/2)(\alpha+2\pi)]}{\sin[(\alpha+2\pi)/2]}$$

$$= \frac{\sin(\alpha+2\pi)}{\sin(\alpha/2+\pi)} = \frac{\sin\alpha\cos2\pi+\sin2\pi\cos\alpha}{\sin(\alpha/2)\cos\pi+\sin\pi\cos(\alpha/2)}$$

$$= \frac{\sin\alpha}{-\sin(\alpha/2)} = \frac{\sin[(\surd 1/2+1/2)\alpha]}{-\sin(\alpha/2)} = -\chi(\alpha) \tag{61}$$

This result, $\chi(\alpha+2\pi) = -\chi(\alpha)$, implies that rotation by 2π is not the identity operation.

After Bethe we solve this difficulty in the following manner. We treat rotation by 2π as a symmetry operation but not as the identity operation. We will call rotation by 2π as simply R.

For each rotation group we must combine R with each of the group rotations. This yields the following classes in 'double' rotation groups:

$$E \tag{62a}$$

$$R \tag{62b}$$

$$C_2 \text{ and } C_2R \tag{62c}$$

$$C_n \text{ and } C_n^{n-1}R \tag{62d}$$

$$C_n^m \text{ and } C_n^{n-m}R \tag{62e}$$

For the double groups (i.e., the groups for which rotation by 2π, R, is considered a symmetry operation different from E). The characters of the new representations are given by

$$\chi(E) = 2J+1 \tag{63a}$$

$$\chi(R) = -(2J+1) \tag{63b}$$

$$\chi(\pi) = 0 \tag{63c}$$

and for other rotations (26) gives the character.

For the rotation double group D_4', we need only consider the rotational subgroup D_4 of D_{4h} to obtain the information we seek, there are the following seven classes.

$$E \qquad (64a)$$

$$R \qquad (64b)$$

$$C_4 \text{ and } C_4^3R \qquad (64c)$$

$$C_4^3 \text{ and } C_4R \qquad (64d)$$

$$C_2 \text{ and } C_2R \qquad (64e)$$

$$2C_2' \text{ and } 2C_2'R \qquad (64f)$$

$$2C_2'' \text{ and } 2C_2''R \qquad (64g)$$

Seven classes means that D_4' will have seven irreducible representations. Five of these are carryovers from D_4 (A_1, A_2, B_1, B_2, and E). It is a requirement that the sum of the squares of the dimensions of the irreducible representations must equal the order (h) of the group. This means that the sixth and seventh irreducible representations of D_4' must be, each, doubly degenerate. We will call these representations Γ_6 and Γ_7.

Using (63a-c) and (26) to derive the characters of Γ_6 and Γ_7 we can construct the character table for D_4'. The character table for D_4' is given in Table 21a.

To determine how the tetragonal levels are perturbed when we add the spin-orbit interaction we must take the direct product of the space and spin part for each level and then decompose the resulting representation into one (or more) of the D_4' irreducible representations.

TABLE 21

a) The Character Table for D_4'

D_4'	E	R	C_4 C_4^3R	C_4^3 C_4R	C_2 C_2R	$2C_2'$ $2C_2'R$	$2C_2''$ $2C_2''R$
$\Gamma_1(A_1)$	1	1	1	1	1	1	1
$\Gamma_2(A_2)$	1	1	1	1	1	-1	-1
$\Gamma_3(B_1)$	1	1	-1	-1	1	1	-1
$\Gamma_4(B_2)$	1	1	-1	-1	1	-1	1
$\Gamma_5(E)$	2	2	0	0	-2	0	0
Γ_6	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
Γ_7	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0

b) Representations of the Doublet (J=1/2) and Quartet (J=3/2) Spin States of d^3 and D_4'

J=1/2	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
J=3/2	4	-4	0	0	0	0	0

The orbital part of each tetragonal level will correspond to one of the Γ_1 through Γ_5 representations of D_4' (i.e., A_1, A_2, B_1, B_2 or E). For the spin part we must construct the representations which correspond to the doublet (J = 1/2) and to the quartet (J = 3/2) spin states. This is done using (63a-c) and (26). These two representations are given in Table 21b. It is apparent that J = 1/2 gives Γ_6 while J = 3/2 gives $\Gamma_6 + \Gamma_7$. That is,

$$\text{doublet } (J = 1/2) = \Gamma_6^Q \tag{65a}$$

$$\text{quartet } (J = 3/2) = \Gamma_6^Q + \Gamma_7^Q \; . \tag{65b}$$

We can now carry out the direct products of space and spin for the tetragonal levels of this coupling scheme. The representations corresponding to these products are given in Table 22a. The decomposition of these products is given in Table 22b. As expected, only Γ_6^Q and Γ_7^Q are obtained since the total momentum is not an integer.

To construct the three electron wave functions for the spin part we must know the transformation properties of α and β under E, $C_4(z)$ and $C_2'(y)$.

The spin components α and β can be described by the row matrix $(\alpha\beta)$. In that case

$$(\alpha\beta)\begin{pmatrix}1\\0\end{pmatrix} = \alpha \tag{66a}$$

and

$$(\alpha\beta)\begin{pmatrix}0\\1\end{pmatrix} = \beta \tag{66b}$$

TABLE 22

a) The Representations Which Correspond to the Direct Products of Space and Spin for the Tetragonal Levels of $\{L,S,\chi^C,\chi^Q,\Gamma^Q\}$

				C_4	C_4^3	C_2	$2C_2'$	$2C_2''$
Tetragonal Level	Direct[k] Product	E	R	C_4^3R	C_4R	C_2R	$2C_2'R$	$2C_2''R$
$^2A_{1g}$	$a_1 \times \Gamma_6$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
$^2A_{2g}$	$a_2 \times \Gamma_6$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
$^2B_{1g}$	$b_1 \times \Gamma_6$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0
$^2B_{2g}$	$b_2 \times \Gamma_6$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0
^2E_g	$e \times \Gamma_6$	4	-4	0	0	0	0	0
$^4A_{2g}$	$a_2 \times \Gamma_6$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
	$a_2 \times \Gamma_7$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0
$^4B_{1g}$	$b_1 \times \Gamma_6$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0
	$b_1 \times \Gamma_7$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0

TABLE 22--Continued

				C_4	C_4^3	C_2	$2C_2'$	$2C_2''$
Tetragonal Level	Direct Product[k]	E	R	C_4^3R	C_4R	C_2R	$2C_2'R$	$2C_2''R$
$^4B_{2g}$	$b_2 x \Gamma_6$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0
	$b_2 x \Gamma_7$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
^4E_g	$e x \Gamma_6$	4	-4	0	0	0	0	0
	$e x \Gamma_7$	4	-4	0	0	0	0	0

[k] In the direct product the orbital part of the wave function is given lower case notation (i.e., a_1, a_2, b_1, b_2, e) while the spin part of the wave function is given gamma notation (i.e., Γ_6 and Γ_7).

TABLE 22--Continued

b) The Decomposition of the Tetragonal Levels of the $\{L,S,\chi^C,\chi^Q,\Gamma^Q\}$ Coupling Scheme When The Spin-Orbit Perturbation is Added

Tetragonal Level	Spin-Orbit Level(s)
$^2A_{1g}$	Γ_6
$^2A_{2g}$	Γ_6
$^2B_{1g}$	Γ_7
$^2B_{2g}$	Γ_7
^2E_g	$\Gamma_6+\Gamma_7$
$^4A_{2g}$	$\Gamma_6+\Gamma_7$
$^4B_{1g}$	$\Gamma_6+\Gamma_7$
$^4B_{2g}$	$\Gamma_6+\Gamma_7$
^4E_g	$2\Gamma_6+2\Gamma_7$

Therefore, we can represent the spins α and β by the matrices $\begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$, respectively.[1]

The transformation of one coordinate system into another can be accomplished by the application of three successive rotations. The three specific angles of rotation are known as the Eulerian angles.[2] We will utilize Goldstein's definition of the Eulerian angles.[3]

The first rotation will be by ϕ degrees about the z axis. The second rotation will be by θ degrees about the x axis generated by the first rotation. The thid rotation will be by ψ degrees about the z axis generated by the second rotation. As always, the rotations are carried out counterclockwise.

The effect of the three rotations on the axes can be described by the following transformation matrices. It is important to note that we have chosen 'replaced by,' not 'goes into,' for the transformation of the axes. That is, in the first rotation by ϕ degrees about the z axis, z is replaced by z_1, x is replaced by x_1, and y is replaced by y_1. Thus, for the three rotations we have

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} , \qquad (67a)$$

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[1] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

[2] Ibid.

[3] Herbert Goldstein, Classical Mechanics, Addison-Wesley Publishing Co., Reading, Mass., 1957.

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \quad \text{and} \qquad (67b)$$

$$\begin{pmatrix} x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}$$

The total change is given by the product of the three matrices which is

$$\begin{pmatrix} x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

This reduces to

$$\begin{pmatrix} \cos\phi\cos\psi-\sin\phi\cos\theta\sin\psi & -\sin\psi\cos\phi-\sin\phi\cos\theta\cos\psi & \sin\phi\sin\theta \\ \sin\phi\cos\psi+\cos\phi\cos\theta\sin\psi & -\sin\phi\sin\psi+\cos\phi\cos\theta\cos\psi & -\sin\theta\cos\phi \\ \sin\theta\sin\psi & \sin\theta\cos\psi & \cos\theta \end{pmatrix} \qquad (68)$$

The above matrix will enable us to determine the Eulerian angles ϕ, θ and ψ for any rotation. This is done by finding the transformation matrix of the rotation for the cartesian coordinates x, y and z and equating it with (68). This procedure will be illustrated shortly.

The spin has two components, α and β. Therefore, in order to determine how the spin transforms under the rotations of D_4 we need to find a way to represent a rotation through the Eulerian angles, a three dimensional rotation, by a two dimension matrix.

Goldstein[1] outlines a procedure for obtaining the 2 x 2 complex Eulerian transformation matrices. We will use these matrices to elucidate the transformation properties of α and β. The matrices are

$$\begin{pmatrix} e^{i\phi/2} & 0 \\ 0 & e^{-i\phi/2} \end{pmatrix} \tag{69a}$$

$$\begin{pmatrix} \cos\theta/2 & i\sin\theta/2 \\ i\sin\theta/2 & \cos\theta/2 \end{pmatrix} \quad \text{and} \tag{69b}$$

$$\begin{pmatrix} e^{i\psi/2} & 0 \\ 0 & e^{-i\psi/2} \end{pmatrix} \tag{69c}$$

for the three Eulerian rotations. The product of the matrices is

$$\begin{pmatrix} e^{i(\phi+\psi)/2} \cdot \cos\theta/2 & ie^{i(\phi-\psi)/2} \cdot \sin\theta/2 \\ ie^{-i(\phi-\psi)/2} \cdot \sin\theta/2 & e^{=i(\varphi+\psi)/2} \cdot \cos\theta/2 \end{pmatrix} \tag{70}$$

Let us now find the above two dimension matrix which will represent $C_4(z)$. The effect of $C_4(z)$ on the cartesian axes is given by

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[1] Herbert Goldstein, Classical Mechanics, Addison-Wesley Publishing Co., 1957.

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} -y \\ x \\ z \end{pmatrix} \qquad (71)$$

Equating this transformation matrix with (68), the matrix which gives the effect of a general rotation in terms of the Eulerian angles, we can obtain ϕ, θ and ψ for $C_4(z)$. Thus, we find

$$\cos\theta = 1.$$

Therefore, θ must be 0 or 2π. Also

$$\cos\phi \cos\psi - \sin\phi \sin\psi = 0,$$

or

$$\cos(\phi+\psi) = 0$$

Hence, $(\phi+\psi)$ must be equal to $\frac{\pi}{2}$. No additional information about the Eulerian angles for $C_4(z)$ can be obtained from the two matrices (71) and (68).

Substituting $\theta = 0$ or 2π and $(\phi+\psi) = \pi/2$ into (70) we obtain for $C_4(z)$ the transformation matrix

$$\begin{pmatrix} \pm e^{i\pi/4} & 0 \\ 0 & \pm e^{-i\pi/4} \end{pmatrix} \qquad (72)$$

By this same approach we can determine the complex two dimensional matrix which represents any rotation of interest. These matrices for E, $C_4(z)$, and $C_2'(y)$ of D_4 are given in Table 23.

TABLE 23

The Complex Two Dimensional Eulerian
Transformation Matrices for E,
$C_4(z)$ and $C_2'(y)$ of D_4
Symmetry

E	$C_4(z)$	$C_2'(y)$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \pm e^{i\pi/4} & 0 \\ 0 & \pm e^{-i\pi/4} \end{pmatrix}$	$\begin{pmatrix} 0 & ie^{i\pi/2} \\ \pm ie^{-i\pi/2} & 0 \end{pmatrix}$

Using the matrices given in Table 23 we can elucidate the transformation properties of α and β. As an example, let us consider the effect of the rotation operation $C_4(z)$ and α and β. For $C_4(z)$ we have

$$C_4(z)\,\alpha = \begin{pmatrix} \pm e^{i\pi/4} & 0 \\ 0 & \pm e^{-i\pi/4} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \pm e^{i\pi/4}\,\alpha$$

and

$$C_4(z)\,\beta = \begin{pmatrix} \pm e^{i\pi/4} & 0 \\ 0 & \pm e^{-i\pi/4} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \pm e^{-i\pi/4}\,\beta \ .$$

Using these results it will be straightforward to obtain the transformation properties of the three electron spin functions. Let us consider $C_4(z)$ on $\alpha\beta\alpha$ as an example.

$$C_4(z)(\alpha\beta\alpha) = (\pm e^{i\pi/4})(\pm e^{-i\pi/4})(\pm e^{i\pi/4})(\alpha\beta\alpha) = e^{i\pi/4}(\alpha\beta\alpha)$$

This procedure allows us to determine the transformation properties of the spin products under all the rotations of the point group of interest. The transformation properties of the three electron spin products for E, $C_4(z)$ and $C_2'(y)$ of D_4 are given in Table 24 along with the transformation properties of α and β for these rotations.

Now we must derive a basis set for both Γ_6^Q and Γ_7^Q before we construct the space and spin combinations. We must have a basis set for these representations in order to determine how the a and b components of each transform under the rotations of interest.

We choose as our basis the following normalized three electron spin functions.

$$\Gamma_{6a}^Q = (\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)/\sqrt{3} \qquad (73a)$$

$$\Gamma_{6b}^Q = (\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3} \qquad (73b)$$

$$\Gamma_{7a}^Q = \alpha\alpha\alpha \qquad (73c)$$

$$\Gamma_{7b}^Q = \beta\beta\beta \qquad (73d)$$

In addition to serving as the basis set for Γ_6^Q and Γ_7^Q (73a-d) are the quartet spin functions.

We can check the legitamcy of (73a-d) as a basis set for Γ_6 and Γ_7 by deriving the representations they generate for $C_4(z)$ and $C_2'(y)$ and comparing the characters of these representations with the

TABLE 24

The Transformation Properties of α and β and the Three Electron Spin Products for E, $(C_4(z)$ and $C_2'(y)$ of D_4 Symmetry

Function	E	$C_4(z)$	$C_2'(y)$
α	α	$\pm e^{i\pi/4}\alpha$	$\pm ie^{i\pi/2}\beta$
β	β	$\pm e^{-i\pi/4}\beta$	$\pm ie^{-i\pi/2}\alpha$
$(\alpha\alpha\alpha)$	$(\alpha\alpha\alpha)$	$e^{3i\pi/4}(\alpha\alpha\alpha)$	$-ie^{3i\pi/2}(\beta\beta\beta)$
$(\beta\beta\beta)$	$(\beta\beta\beta)$	$e^{-3i\pi/4}(\beta\beta\beta)$	$-ie^{-3i\pi/2}(\alpha\alpha\alpha)$
$(\alpha\alpha\beta)$	$(\alpha\alpha\beta)$	$e^{i\pi/4}(\alpha\alpha\beta)$	$-ie^{i\pi/2}(\beta\beta\alpha)$
$(\alpha\beta\alpha)$	$(\alpha\beta\alpha)$	$e^{i\pi/4}(\alpha\beta\alpha)$	$-ie^{i\pi/2}(\beta\alpha\beta)$
$(\beta\alpha\alpha)$	$(\beta\alpha\alpha)$	$e^{i\pi/4}(\beta\alpha\alpha)$	$-ie^{i\pi/2}(\alpha\beta\beta)$
$(\beta\beta\alpha)$	$(\beta\beta\alpha)$	$e^{-i\pi/4}(\beta\beta\alpha)$	$-ie^{-i\pi/2}(\alpha\alpha\beta)$
$(\beta\alpha\beta)$	$(\beta\alpha\beta)$	$e^{-i\pi/4}(\beta\alpha\beta)$	$-ie^{-i\pi/2}(\alpha\beta\alpha)$
$(\alpha\beta\beta)$	$(\alpha\beta\beta)$	$e^{-i\pi/4}(\alpha\beta\beta)$	$-ie^{-i\pi/2}(\beta\alpha\alpha)$

known characters of Γ_6 and Γ_7 for $C_4(z)$ and $C_2{}'(y)$ (cf. Table 20). This is done in Table 25.

The orbital transformation properties and the necessary basis are listed in Table 26.

Now we can form the appropriate space and spin combinations which transform as the irreducible representations of $D_4{}'$. These are listed in Table 27.

To obtain the doublet spin-adapted functions in microstate form we substitute directly the cubic oriented spherical harmonics from Table 17 when Γ^S_{6a} is called for. This is so because in writing down the cubic oriented spherical harmonics in microstate form we always chose the $|L,S;M_L,M_S>$ functions with $M_S = 1/2$ which corresponds to Γ^S_{6a}. When Γ^S_{6b} is called for we must substitute the $|L,S;M_L,M_S>$ functions with $M_S = -1/2$ from Table 6 into the generalized cubic oriented spherical harmonics given in Table 15.

To illustrate how we obtain the quartet spin-adapted functions in microstate form let us take ${}^4B_{1g}{}^Q$ as an example. We will consider only the a component of $\Gamma_7{}^Q$ in this example. Thus, we have

$$\Gamma^Q_{7a}\{{}^4B_{1g}{}^Q[{}^4A_{2g}{}^C({}^4F)]\} = b_1{}^Q\Gamma^S_{6b} \ .$$

To obtain this function we take the ${}^4A_{2g}{}^C$ function of ${}^4F$ from Table 17 void of spin and fix to it the Γ^S_{6b} function (73b).

$$\Gamma^Q_{7a}\{{}^4B_{1g}{}^Q[{}^4A_{2g}{}^C({}^4F)]\} = i[(1\text{-}1\text{-}2)-(21\text{-}1]\cdot(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)\sqrt{6}$$

$$= i[(\bar{1}\text{-}\bar{1}\text{-}2) + (\bar{1}\text{-}1\text{-}\bar{2}) + (1\text{-}\bar{1}\text{-}\bar{2}) - (\bar{2}\bar{1}\text{-}1) - (\bar{2}1\text{-}\bar{1}) - (2\bar{1}\text{-}\bar{1})]/\sqrt{6} \ .$$

TABLE 25

Check of the Transformation Properties of $\Gamma^{Q}_{6a,b}$ and $\Gamma^{Q}_{7a,b}$

Basis	$C_4(Z)$	$C_2'(Y)$
$\Gamma^{Q}_{6a} = (\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)/\sqrt{3}$	$(\sqrt{2}/2)(1+i)\Gamma^{Q}_{6a}$	$-i\Gamma^{Q}_{6b}$
$\Gamma^{Q}_{6b} = (\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	$(\sqrt{2}/2)(1-i)\Gamma^{Q}_{6b}$	$-i\Gamma^{Q}_{6a}$
χ of Γ_6^{Q}	$\sqrt{2}$	0
$\Gamma^{Q}_{7a} = \alpha\alpha\alpha$	$(\sqrt{2}/2)(i-1)\Gamma^{Q}_{7a}$	$-i\Gamma^{Q}_{7b}$
$\Gamma^{Q}_{7b} = \beta\beta\beta$	$(\sqrt{2}/2)(-i-1)\Gamma^{Q}_{7b}$	$-i\Gamma^{Q}_{7a}$
χ of Γ_7^{Q}	$-\sqrt{2}$	0

TABLE 26

The Transformation Properties of the Orbital Functions for $C_4(Z)$ and $C_2'(Y)$ of D_4' Symmetry

Representation[k]	Basis	$C_4(Z)$	$C_2'(Y)$
a_1	--	a_1	a_1
a_2	--	a_2	$-a_2$
b_1	--	$-b_1$	b_1
b_2	--	$-b_2$	$-b_2$
$e_a(t_1)$	y	e_b	e_a
$e_b(t_1)$	x	$-e_a$	$-e_b$
$e_a(t_2)$	xz	$-e_b$	e_a
$e_b(t_2)$	yz	e_a	$-e_b$

---

[k] Two sets of basis are listed for e. One set for the e state derived from cubic t_1 and one set for the e state derived from cubic t_2.

TABLE 27

The Space and Spin Combinations[k] Which Form the Wave Functions for the Spin-Orbit Perturbation of the $\{L,S,X^C,X^Q,\Gamma^Q\}$ Coupling Scheme

${}^2A^Q_{1g}$
$\Gamma_{6a} = a_1\Gamma_{6a}$ $\Gamma_{6b} = a_1\Gamma_{6b}$
${}^2A^Q_{2g}$
$\Gamma_{6a} = a_2\Gamma_{6a}$ $\Gamma_{6b} = -a_2\Gamma_{6b}$
${}^2B^Q_{1g}$
$\Gamma_{7a} = b_1\Gamma_{6b}$ $\Gamma_{7b} = b_1\Gamma_{6a}$
${}^2B^Q_{2g}$
$\Gamma_{7a} = -b_2\Gamma_{6b}$ $\Gamma_{7b} = b_2\Gamma_{6a}$
${}^2E^Q_g({}^2T^C_{1g})$
$\Gamma_{6a} = (-ie_a\Gamma_{6b}-e_b\Gamma_{6b})/\sqrt{2}$ $\Gamma_{6b} = (ie_a\Gamma_{6a}-e_b\Gamma_{6a})/\sqrt{2}$

TABLE 27--Continued

$\Gamma_{7a} = (ie_a\Gamma_{6a}+e_b\Gamma_{6a})/\sqrt{2}$

$\Gamma_{7b} = (-ie_a\Gamma_{6b}+e_b\Gamma_{6b})/\sqrt{2}$

$^2E_g^Q(^2T_{2g}^C)$

$\Gamma_{6a} = (-ie_a\Gamma_{6b}+e_b\Gamma_{6b})/\sqrt{2}$

$\Gamma_{6b} = (-ie_a\Gamma_{6a}-e_b\Gamma_{6a})/\sqrt{2}$

$\Gamma_{7a} = (ie_a\Gamma_{6a}-e_b\Gamma_{6a})/\sqrt{2}$

$\Gamma_{7b} = (ie_a\Gamma_{6b}+e_b\Gamma_{6b})/\sqrt{2}$

$^4A_{2g}^Q$

$\Gamma_{6a} = a_2\Gamma_{6a}$ $\quad\quad$ $\Gamma_{7a} = a_2\Gamma_{7a}$

$\Gamma_{6b} = -a_2\Gamma_{6b}$ $\quad\quad$ $\Gamma_{7b} = -a_2\Gamma_{7b}$

$^4B_{1g}^Q$

$\Gamma_{6a} = b_1\Gamma_{7b}$ $\quad\quad$ $\Gamma_{7a} = b_1\Gamma_{6b}$

$\Gamma_{6b} = b_1\Gamma_{7a}$ $\quad\quad$ $\Gamma_{7b} = b_1\Gamma_{6a}$

$^4B_{2g}$

$\Gamma_{6a} = -b_2\Gamma_{7b}$ $\quad\quad$ $\Gamma_{7a} = -b_2\Gamma_{6b}$

$\Gamma_{6b} = b_2\Gamma_{7a}$ $\quad\quad$ $\Gamma_{7b} = b_2\Gamma_{6a}$

TABLE 27--Continued

${}^4E_g^Q({}^4T_{1g}^C)$
$\Gamma_{6a}(1) = (-ie_a\Gamma_{6b}-e_b\Gamma_{6b})/\sqrt{2}$
$\Gamma_{6b}(1) = (ie_a\Gamma_{6a}+e_b\Gamma_{6a})/\sqrt{2}$
$\Gamma_{6a}(2) = (e_a\Gamma_{7a}+ie_b\Gamma_{7a})/\sqrt{2}$
$\Gamma_{6b}(2) = (-e_a\Gamma_{7b}+ie_b\Gamma_{7b})/\sqrt{2}$
$\Gamma_{7a}(1) = (ie_a\Gamma_{6a}+e_b\Gamma_{6a})/\sqrt{2}$
$\Gamma_{7b}(1) = (-ie_a\Gamma_{6b}+e_b\Gamma_{6b})/\sqrt{2}$
$\Gamma_{7a}(2) = (-ie_a\Gamma_{7b}+e_b\Gamma_{7b})/\sqrt{2}$
$\Gamma_{7b}(2) = (ie_a\Gamma_{7a}+e_b\Gamma_{7a})/\sqrt{2}$
${}^4E_g^Q({}^4T_{2g}^C)$
$\Gamma_{6a}(1) = (-ie_a\Gamma_{6b}+e_b\Gamma_{6b})/\sqrt{2}$
$\Gamma_{6b}(1) = (-ie_a\Gamma_{6a}-e_b\Gamma_{6a})/\sqrt{2}$
$\Gamma_{6a}(2) = (e_a\Gamma_{7a}-ie_b\Gamma_{7a})/\sqrt{2}$
$\Gamma_{6b}(2) = (e_a\Gamma_{7b}+ie_b\Gamma_{7b})/\sqrt{2}$

TABLE 27--Continued

$\Gamma_{7a}(1) = (ie_a\Gamma_{6a}-e_b\Gamma_{6a})/\sqrt{2}$

$\Gamma_{7b}(1) = (ie_a\Gamma_{6b}+e_b\Gamma_{6b})/\sqrt{2}$

$\Gamma_{7a}(2) = (-ie_a\Gamma_{7b}-e_b\Gamma_{7b})/\sqrt{2}$

$\Gamma_{7b}(2) = (-ie_a\Gamma_{7a}+e_b\Gamma_{7a})/\sqrt{2}$

---

[k] In the product of space and spin the orbital part of the wave function is given lower case notation (i.e., a_1, a_2, b_1, b_2, e, t_1 and t_2) while the spin part of the wave function is given gamma notation (i.e., Γ_6 and Γ_7).

Following these procedures for doublets and quartets we can easily write down the spin-adapted wave functions for $\Gamma_6{}^Q$ and $\Gamma_7{}^Q$. The a components of $\Gamma_6{}^Q$ and $\Gamma_7{}^Q$ in microstate form are given in Table 28.

The spin-orbit perturbation has block diagonalized the secular determinant into two 30 x 30 sections, $\Gamma_6{}^Q$ and $\Gamma_7{}^Q$. This is illustrated in Fig. 8.

An important result of spin-adapting is the mixing of the wave functions such that quadrate representations with different spin multiplicities may then belong to the same irreducible representations. Therefore, after spin-adaption, within each irreducible representation there may exist non-zero off-diagonal matrix elements between doublet and quartet states. The appearance of the low intensity spin-forbidden bands in the ligand field spectra of transition metal compounds is experimental evidence that this mixing of different spin states occurs.

As given by Condon and Shortley[1] and derived by Thomas[2] and Frenkel[3] the single electron Hamiltonian due to the interaction of the magnetic fields generated by the spin and the orbital momentum of the electron is

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[1] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, University Press, Cambridge, 1951.

[2] L. H. Thomas, Nature, 117, 514 (1926).

[3] J. Frenkel, Zeits für Phys., 37, 243 (1926)

Γ_6^Q 30x30	0
0	Γ_7^Q 30x30

Figure 8. The Spin-Orbit Secular Determinant for d^3 for the $\{L,S,X^C,X^Q,\Gamma^Q\}$ Coupling Scheme.

TABLE 28

a) Numbering of the Eigenvectors of the $\{L,S,X^C,X^Q,\Gamma^Q\}$ Coupling Scheme

---

$\Gamma_6{}^Q$

---

(1) = $^2A^Q_{1g}(^2E^C_g(^2D\text{-}a))$

(2) = $^2A^Q_{1g}(^2E^C_g(^2D\text{-}b))$

(3) = $^2A^Q_{1g}(^2A^C_{1g}(^2G))$

(4) = $^2A^Q_{1g}(^2E^C_g(^2G))$

(5) = $^2A^Q_{1g}(^2E^C_g(^2H))$

(6) = $^2A^Q_{2g}(^2T^C_{1g}(^2P))$

(7) = $^2A^Q_{2g}(^2T^C_{1g}(^2F))$

(8) = $^2A^Q_{2g}(^2T^C_{1g}(^2G))$

(9) = $^2A^Q_{2g}(^2T^C_{1g}\text{-}1(^2H))$

(10) = $^2A^Q_{2g}(^2T^C_{1g}\text{-}2(^2H))$

(11) = $^2E^Q_g(^2T^C_{1g}(^2P))$

(12) = $^2E^Q_g(^2T^C_{2g}(^2D\text{-}a))$

(13) = $^2E^Q_g(^2T^C_{2g}(^2D\text{-}b))$

(14) = $^2E^Q_g(^2T^C_{1g}(^2F))$

(15) = $^2E^Q_g(^2T^C_{2g}(^2F))$

(16) = $^2E^Q_g(^2T^C_{1g}(^2G))$

(17) = $^2E^Q_g(^2T^C_{2g}(^2G))$

(18) = $^2E^Q_g(^2T^C_{2g}(^2H))$

(19) = $^2E^Q_g(^2T^C_{1g}\text{-}1(^2H))$

(20) = $^2E^Q_g(^2T^C_{1g}\text{-}2(^2H))$

(21) = $^4A^Q_{2g}(^4T^C_{1g}(^4P))$

(22) = $^4A^Q_{2g}(^4T^C_{1g}(^4F))$

(23) = $^4B^Q_{1g}(^4A^C_{2g}(^4F))$

(24) = $^4B^Q_{2g}(^4T^C_{2g}(^4F))$

(25) = $(1)^4E^Q_g(^4T^C_{1g}(^4P))$

(26) = $(2)^4E^Q_g(^4T^C_{1g}(^4P))$

(27) = $(1)^4E^Q_g(^4T^C_{1g}(^4F))$

(28) = $(2)^4E^Q_g(^4T^C_{1g}(^4F))$

TABLE 28--Continued

$(29) = (1)\,{}^4E_g^Q({}^4T_{2g}^C({}^4F))$

$(30) = (2)\,{}^4E_g^Q({}^4T_{2g}^C({}^4F))$

Γ_7^Q

$(1) = {}^2B_{1g}^Q({}^2E_g^C({}^2D\text{-a}))$

$(2) = {}^2B_{1g}^Q({}^2E_g^C({}^2D\text{-b}))$

$(3) = {}^2B_{1g}^Q({}^2A_{2g}^C({}^2F))$

$(4) = {}^2B_{1g}^Q({}^2E_g^C({}^2G))$

$(5) = {}^2B_{1g}^Q({}^2E_g^C({}^2H))$

$(6) = {}^2E_g^Q({}^2T_{1g}^C({}^2P))$

$(7) = {}^2E_g^Q({}^2T_{1g}^C({}^2F))$

$(8) = {}^2E_g^Q({}^2T_{1g}^C({}^2G))$

$(9) = {}^2E_g^Q({}^2T_{1g}^C\text{-}1({}^2H))$

$(10) = {}^2E_g^Q({}^2T_{1g}^C\text{-}2({}^2H))$

$(11) = {}^2E_g^Q({}^2T_{2g}^C({}^2D\text{-a}))$

$(12) = {}^2E_g^Q({}^2T_{2g}^C({}^2D\text{-b}))$

$(13) = {}^2E_g^Q({}^2T_{2g}^C({}^2F))$

$(14) = {}^2E_g^Q({}^2T_{2g}^C({}^2G))$

$(15) = {}^2E_g^Q({}^2T_{2g}^C({}^2H))$

$(16) = {}^2B_{2g}^Q({}^2T_{2g}^C({}^2F))$

$(17) = {}^2B_{2g}^Q({}^2T_{2g}^C({}^2H))$

$(18) = {}^2B_{2g}^Q({}^2T_{2g}^C({}^2G))$

$(19) = {}^2B_{2g}^Q({}^2T_{2g}^C({}^2D\text{-a}))$

$(20) = {}^2B_{2g}^Q({}^2T_{2g}^C({}^2D\text{-b}))$

$(21) = {}^4A_{2g}^Q({}^4T_{1g}^C({}^4P))$

$(22) = {}^4A_{2g}^Q({}^4T_{1g}^C({}^4F))$

$(23) = {}^4B_{1g}^Q({}^4A_{2g}^C({}^4F))$

$(24) = {}^4B_{2g}^Q({}^4T_{2g}^C({}^4F))$

$(25) = (1)\,{}^4E_g^Q({}^4T_{1g}^C({}^4P))$

$(26) = (2)\,{}^4E_g^Q({}^4T_{1g}^C({}^4P))$

TABLE 28--Continued

(27) = $(1)^4E_g^Q(^4T_{1g}^C(^4F))$

(28) - $(2)^4E_g^Q(^4T_{1g}^C(^4F))$

(29) = $(1)^4E_g^Q(^4T_{2g}^C(^4F))$

(30) = $(2)^4E_g^Q(^4T_{2g}^C(^4F))$

b) The Spin-Adapted Wave Function in Microstate Form
for the $\{L,S,X^C,X^Q,\Gamma^Q\}$ Coupling
Scheme (a component only)

Γ_{6a}^Q

(1) = $((10-\bar{1})+(\bar{2}0-2)-(\bar{1}0-1)-(20-\bar{2}))/2$

(2) = $(3(20-\bar{2})-2\sqrt{6}(1\bar{1}-2)-3(\bar{2}0-2)-3(\bar{1}0-1)$

$+ 3(10-\bar{1})-2\sqrt{6}(2-1-\bar{1}))/\sqrt{84}$

(3) = $(2(10-\bar{1})+\sqrt{6}(2-1-\bar{1})+2(20-\bar{2})-2(\bar{1}0-1)$

$+ \sqrt{6}(1\bar{1}-2)+2(0-2-\bar{2})+\sqrt{6}(-1-\bar{1}-2)-2(\bar{2}0-2)+2(2\bar{2}0)+\sqrt{6}(21\bar{1}))/4\sqrt{3}$

(4) = $(10(10-\bar{1})+5\sqrt{6}(2-1-\bar{1})+10(20-\bar{2})$

$- 10(\bar{1}0-1)+5\sqrt{6}(1\bar{1}-2)-10(\bar{2}0-2)-14(2\bar{2}0)-7\sqrt{6}(21\bar{1})$

$- 7\sqrt{6}(-1-\bar{1}-2)-14(0-2-\bar{2}))/4\sqrt{105}$

(5) = $i(-3(2\bar{2}0)+\sqrt{6}(21\bar{1})-3(0-2-\bar{2})$

$+ \sqrt{6}(-1-\bar{1}-2))/\sqrt{30}$

(6) = $(-4(20-\bar{2})-3\sqrt{6}(1\bar{1}-2)+8(2\bar{0}-2)-4(\bar{2}0-2)$

$- (10-\bar{1})+3\sqrt{6}(2-1-\bar{1})+2(1\bar{0}-1)-(\bar{1}0-1))/\sqrt{210}$

(7) = $(2(\bar{1}0-1)-4(1\bar{0}-1)+\sqrt{6}(1\bar{1}-2)-\sqrt{6}(2-1-\bar{1})$

$+ 4(2\bar{0}-2)-2(\bar{2}0-2)+2(10-\bar{1})-2(20-\bar{2}))/\sqrt{60}$

(8) = $i(3(-1-\bar{1}-2)+\sqrt{6}(0-2-\bar{2})-\sqrt{6}(2\bar{2}0)$

$- 3(31\bar{1}))/\sqrt{30}$

TABLE 28--Continued

$(9) = (4(1\bar{0}-1)-2(\bar{1}0-1)+\sqrt{6}(1\bar{1}-2)-\sqrt{6}(2-1-\bar{1})$

$- (20-\bar{2})+2(2\bar{0}-2)-(\bar{2}0-2)-2(10-\bar{1}))/\sqrt{42}$

$(10) = (3(2\bar{2}0)-\sqrt{6}(21\bar{1})-3(0-2-\bar{2})$

$+ \sqrt{6}(-1-\bar{1}-2))/\sqrt{30}$

$(11) = (-2\sqrt{6}(\bar{2}1-\bar{2})-2\sqrt{6}(2\bar{1}-\bar{2})+4\sqrt{6}(\bar{2}\bar{1}-2)+10(2\bar{0}-\bar{1})$

$- 8(\bar{2}\bar{0}-1)-2(\bar{2}0-\bar{1})-3\sqrt{6}(1\bar{1}-\bar{1})-3\sqrt{6}(\bar{1}0\bar{0}))/\sqrt{420}$

$(12) = i((1\bar{1}-\bar{1})+(\bar{1}0\bar{0})+(\bar{2}\bar{1}-2)-(2\bar{1}-\bar{2}))/2$

$(13) = i(4(\bar{2}1-\bar{2})-3(\bar{2}\bar{1}-2)-(2\bar{1}-\bar{2})-(1\bar{1}-\bar{1})$

$+ 3(\bar{1}0\bar{0})-2\sqrt{6}(\bar{2}0-\bar{1})+2\sqrt{6}(2\bar{0}-\bar{1}))/\sqrt{84}$

$(14) = (2\sqrt{6}(1\bar{1}-\bar{1})-3(\bar{2}\bar{0}-1)-\sqrt{6}(\bar{2}\bar{1}-2)-2\sqrt{6}(2\bar{1}-\bar{2})$

$+ 3\sqrt{6}(\bar{2}1-\bar{2})-3\sqrt{6}(\bar{1}0\bar{0})+3(\bar{2}0-\bar{1})-5(\bar{0}-1-\bar{2})-5(0-\bar{1}-\bar{2})$

$+ 10(\bar{0}-\bar{1}-2)+5\sqrt{6}(\bar{1}-2-\bar{2}))/4\sqrt{30}$

$(15) = -(2\sqrt{6}(1\bar{1}-\bar{1})-3(\bar{2}\bar{0}-1)-\sqrt{6}(\bar{2}\bar{1}-2)$

$- 2\sqrt{6}(2\bar{1}-\bar{2})+3\sqrt{6}(\bar{2}1-\bar{2})-3\sqrt{6}(\bar{1}0\bar{0})+3(\bar{2}0-\bar{1})+3(0-\bar{1}-\bar{2})$

$- 6(\bar{0}-\bar{1}-2)-3\sqrt{6}(\bar{1}-2-\bar{2})+3(\bar{0}-1-\bar{2}))/12\sqrt{2}$

$(16) = i(\sqrt{6}(\bar{1}0\bar{0})-7(\bar{2}\bar{0}-1)+3(\bar{2}\bar{0}-1)+4(2\bar{0}-\bar{1})$

$+ 3(0-\bar{1}-\bar{2})+2\sqrt{6}(2\bar{1}-\bar{2})+2\sqrt{6}(1\bar{1}-\bar{1})-\sqrt{6}(\bar{2}\bar{1}-2)-\sqrt{6}(\bar{2}1-\bar{2})$

$+ \sqrt{6}(\bar{1}-2-\bar{2})-2(\bar{0}-\bar{1}-2)-(\bar{0}-1-\bar{2}))/4\sqrt{10}$

$(17) = i(-\sqrt{6}(\bar{1}0\bar{0})+7(\bar{2}\bar{0}-1)-3(\bar{2}0-\bar{1})-4(2\bar{0}-\bar{1})$

$- 2\sqrt{6}(2\bar{1}-\bar{2})-2\sqrt{6}(1\bar{1}-\bar{1})+\sqrt{6}(\bar{2}\bar{1}-2)+\sqrt{6}(\bar{2}1-\bar{2})+21(0-\bar{1}-\bar{2})$

$+ 7\sqrt{6}(\bar{1}-2-\bar{2})-14(\bar{0}-\bar{1}-2)-7(\bar{0}-1-\bar{2}))/4\sqrt{70}$

$(18) = (15(2\bar{2}\bar{1})-8(1\bar{1}-\bar{1})+6(\bar{1}0\bar{0})-2\sqrt{6}(\bar{2}\bar{0}-1)$

$- \sqrt{6}(2\bar{0}-\bar{1})+3\sqrt{6}(\bar{2}0-\bar{1})+4(\bar{2}1-\bar{2})-(\bar{2}\bar{1}-2)-3(2\bar{1}-\bar{2})$

$- \sqrt{6}(\bar{0}-\bar{1}-2)-\sqrt{6}(0-\bar{1}-\bar{2})+2\sqrt{6}(\bar{0}-1-\bar{2})+3(\bar{1}-2-\bar{2}))/4\sqrt{30}$

TABLE 28--Continued

$(19) = (21\sqrt{3}(2\bar{2}\bar{1})+8\sqrt{3}(1\bar{1}-\bar{1})-6\sqrt{3}(\bar{1}0\bar{0})$

$+ 6\sqrt{2}(\bar{2}\bar{0}-1)+3\sqrt{2}(2\bar{0}-\bar{1})-9\sqrt{2}(\bar{2}0-\bar{1})-4\sqrt{3}(\bar{2}1-\bar{2})$

$+ \sqrt{3}(\bar{2}\bar{1}-2)+3\sqrt{3}(2\bar{1}-\bar{2})+7\sqrt{2}(\bar{0}-\bar{1}-2)+7\sqrt{2}(0-\bar{1}-\bar{2})$

$- 14\sqrt{2}(\bar{0}-1-\bar{2})-7\sqrt{3}(\bar{1}-2-\bar{2}))/8\ 42$

$(20) = (5(2\bar{2}\bar{1})+8(1\bar{1}-\bar{1})-6(\bar{1}0\bar{0})+2\sqrt{6}(\bar{2}\bar{0}-1)$

$+ \sqrt{6}(2\bar{0}-\bar{1})-3\sqrt{6}(\bar{2}0-\bar{1})-4(\bar{2}1-\bar{2})+(\bar{2}\bar{1}-2)+3(2\bar{1}-\bar{2})$

$- 3\sqrt{6}(\bar{0}-\bar{1}-2)-3\sqrt{6}(0-\bar{1}-\bar{2})+6\sqrt{6}(\bar{0}-1-\bar{2})+9(\bar{1}-2-\bar{2}))/8\sqrt{10}$

$(21) = (2(10-\bar{1})+2(1\bar{0}-1)+2(\bar{1}0-1)-(20-\bar{2})$

$- (2\bar{0}-2)-(\bar{2}0-2))/\sqrt{15}$

$(22) = ((10-\bar{1})+(1\bar{0}-1)+(\bar{1}0-1)+2(20-\bar{2})$

$+ 2(2\bar{0}-2)+2(\bar{2}0-2))/\sqrt{15}$

$(23) = i((\bar{1}-\bar{1}-\bar{2})-(\bar{2}\bar{1}-\bar{1}))/\sqrt{2}$

$(24) = (-(\bar{1}-\bar{1}-\bar{2})-(\bar{2}\bar{1}-\bar{1}))/\sqrt{2}$

$(25) = (2(2\bar{0}-\bar{1})+2(\bar{2}\bar{0}-1)+2(\bar{2}0-\bar{1})$

$- \sqrt{5}(2\bar{1}-\bar{2})-\sqrt{6}(\bar{2}1-\bar{2})-\sqrt{6}(\bar{2}\bar{1}-2))/\sqrt{30}$

$(26) = i(2(10-2)-\sqrt{6}(2-1-2))/\sqrt{10}$

$(27) = (-3(2\bar{0}-\bar{1})-3(\bar{2}\bar{0}-1)-3(\bar{2}0-\bar{1})-5(\bar{0}-\bar{1}-2)$

$- \sqrt{6}(2\bar{1}-\bar{2})-\sqrt{6}(\bar{2}\bar{1}-2)-\sqrt{6}(\bar{2}1-\bar{2})-5(0-\bar{1}-\bar{2})-5(\bar{0}-1-\bar{2}))/2\sqrt{30}$

$(28) = i(-3(10-2)-\sqrt{6}(2-1-2)-5(210))/\sqrt{40}$

$(29) = (\sqrt{3}(\bar{2}\bar{0}-1)+\sqrt{3}(\bar{2}0-\bar{1})+\sqrt{3}(2\bar{0}-\bar{1})+\sqrt{2}(\bar{2}\bar{1}-2)$

$+ \sqrt{2}(\bar{2}1-\bar{2})+\sqrt{2}(2\bar{1}-\bar{2})-\sqrt{3}(\bar{0}-\bar{1}-2)-\sqrt{3}(0-\bar{1}-\bar{2})-\sqrt{3}(\bar{0}-1-\bar{2}))/2\sqrt{6}$

$(30) = i(-\sqrt{6}(210)+\sqrt{6}(10-2)+2(2-1-2))/4$

TABLE 28--Continued

Γ_7^{Q}

$(1) = (-(\bar{2}\bar{1}\text{-}1)-(\bar{2}0\bar{0})+(2\bar{2}\text{-}\bar{2})+(\bar{2}1\text{-}\bar{1})$

$\quad - (\bar{1}\text{-}1\text{-}\bar{2})-(0\bar{0}\text{-}\bar{2})+(\bar{2}\text{-}2\text{-}\bar{2})+(1\text{-}\bar{1}\text{-}\bar{2}))/\sqrt{8}$

$(2) = (-4(2\bar{1}\text{-}\bar{1})+5(2\bar{2}\text{-}\bar{2})+3(\bar{2}\bar{1}\text{-}1)+(\bar{2}1\text{-}\bar{1})$

$\quad + 3(\bar{2}0\bar{0})+2\sqrt{6}(1\bar{1}\bar{0})-(\bar{1}\text{-}1\text{-}\bar{2})-3(1\text{-}\bar{1}\text{-}\bar{2})+5(\bar{2}\text{-}2\text{-}\bar{2})$

$\quad + 3(0\bar{0}\text{-}\bar{2})+4(\bar{1}\text{-}\bar{1}\text{-}2)+2\sqrt{6}(\bar{0}\text{-}1\text{-}\bar{1}))/2\sqrt{42}$

$(3) = i((\bar{2}\bar{1}\text{-}1)+2(2\bar{2}\text{-}\bar{2})-\sqrt{6}(1\bar{1}\bar{0})-(\bar{2}\bar{1}\text{-}\bar{1})$

$\quad - \sqrt{6}(\bar{0}\text{-}1\text{-}\bar{1})-(1\text{-}\bar{1}\text{-}\bar{2})+2(\bar{2}\text{-}2\text{-}\bar{2})+(\bar{1}\text{-}1\text{-}\bar{2}))/2\sqrt{6}$

$(4) = (4\sqrt{6}(\bar{2}0\bar{0})+4\sqrt{6}(2\bar{1}\text{-}\bar{1})+2(1\bar{1}\bar{0})$

$\quad - 3\sqrt{6}(\bar{2}\bar{1}\text{-}1)-\sqrt{6}(\bar{2}1\text{-}\bar{1})+2\sqrt{6}(2\bar{2}\text{-}\bar{2})+2(\bar{0}\text{-}1\text{-}\bar{1})+\sqrt{6}(\bar{1}\text{-}1\text{-}\bar{2})$

$\quad + 3\sqrt{6}(1\text{-}\bar{1}\text{-}\bar{2})+2\sqrt{6}(\bar{2}\text{-}2\text{-}\bar{2})+4\sqrt{6}(0\bar{0}\text{-}\bar{2})-4\sqrt{6}(\bar{1}\text{-}\bar{1}\text{-}2))/4\sqrt{35}$

$(5) = -i(\sqrt{6}(1\bar{1}\bar{0})-3(\bar{2}0\bar{0})-3(\bar{2}1\text{-}\bar{1})+(\bar{2}\bar{1}\text{-}1)$

$\quad + 2(2\bar{1}\text{-}\bar{1})+(2\bar{2}\text{-}\bar{2})+\sqrt{6}(\bar{0}\text{-}1\text{-}\bar{1})-3(0\bar{0}\text{-}\bar{2})+3(\bar{1}\text{-}1\text{-}\bar{2})-2(\bar{1}\text{-}\bar{1}\text{-}2)$

$\quad - (1\text{-}\bar{1}\text{-}\bar{2})+(\bar{2}\text{-}2\text{-}\bar{2}))/\sqrt{60}$

$(6) = (12(21\text{-}\bar{2})-6(2\bar{1}\text{-}2)-6(\bar{2}1\text{-}2)-4\sqrt{6}(20\text{-}\bar{1})$

$\quad - \sqrt{6}(2\bar{0}\text{-}1)+5\sqrt{6}(\bar{2}0\text{-}1)+9(1\bar{1}\text{-}1)+9(10\bar{0}))/3\sqrt{70}$

$(7) = (-2\sqrt{6}(1\bar{1}\text{-}1)+3(2\bar{0}\text{-}1)+3\sqrt{6}(2\bar{1}\text{-}2)$

$\quad - 2\sqrt{6}(\bar{2}1\text{-}2)+3\sqrt{6}(10\bar{0})-3(20\text{-}\bar{1})-\sqrt{6}(21\text{-}\bar{2})+10(0\text{-}1\text{-}\bar{2})$

$\quad - 5(0\text{-}\bar{1}\text{-}2)-5\sqrt{6}(1\text{-}2\text{-}\bar{2})-5(\bar{0}\text{-}1\text{-}2))/4\sqrt{30}$

$(8) = -i(\sqrt{6}(10\bar{0})-3(2\bar{0}\text{-}1)+7(20\text{-}\bar{1})$

$\quad + \sqrt{6}(21\text{-}\bar{2})+2\sqrt{6}(1\bar{1}\text{-}1)-4(\bar{2}0\text{-}1)-2\sqrt{6}(\bar{2}1\text{-}2)+\sqrt{6}(2\bar{1}\text{-}2)$

$\quad + (0\text{-}\bar{1}\text{-}2)+2(0\text{-}1\text{-}\bar{2})+\sqrt{6}(1\text{-}2\text{-}\bar{2})-3(\bar{0}\text{-}1\text{-}2))/4\sqrt{10}$

TABLE 28--Continued

$$(9) = (-63(2\bar{2}1)-14\sqrt{6}(0-\bar{1}-2)+7\sqrt{6}(0-1-\bar{2})$$
$$+\ 7\sqrt{6}(\bar{0}-1-2)+21(1-2-\bar{2})-24(1\bar{1}-1)+18(10\bar{0})-9\sqrt{6}(2\bar{0}-1)$$
$$+\ 6\sqrt{6}(20-\bar{1})+3(21-\bar{2})-12(2\bar{1}-2)+3\sqrt{6}(\bar{2}0-1)+9(\bar{2}1-2))/24\sqrt{14}$$

$$(10) = (-15(2\bar{2}1)+18\sqrt{6}(0-\bar{1}-2)-9\sqrt{6}(0-1-\bar{2})$$
$$-\ 9\sqrt{6}(\bar{0}-1-2)-27(1-2-\bar{2})-24(1\bar{1}-1)+18(10\bar{0})-9\sqrt{6}(2\bar{0}-1)$$
$$+\ 6\sqrt{6}(20-\bar{1})+3(21-\bar{2})-12(2\bar{1}-2)+3\sqrt{6}(\bar{2}0-1)+9(\bar{2}1-2))/24\sqrt{10}$$

$$(11) = i(-(1\bar{1}-1)-(10\bar{0})-(\bar{2}1-2)+(21-\bar{2}))/2$$

$$(12) = i(-3(21-\bar{2})-(\bar{2}1-2)+4(2\bar{1}-2)+(1\bar{1}-1)$$
$$-\ 3(10\bar{0})+2\sqrt{6}(\bar{2}0-1)-2\sqrt{6}(2\bar{0}-1))/\sqrt{84}$$

$$(13) = -(-4(1\bar{1}-1)+\sqrt{6}(2\bar{0}-1)+6(2\bar{1}-2)$$
$$-\ 4(\bar{2}1-2)+6(10\bar{0})-\sqrt{6}(20-\bar{1})-2(21-\bar{2})-2\sqrt{6}(0-1-\bar{2})$$
$$+\sqrt{6}(0-\bar{1}-2)+6(1-2-\bar{2})+\sqrt{6}(\bar{0}-1-2))/8\sqrt{3}$$

$$(14) = i(\sqrt{6}(10\bar{0})-3(2\bar{0}-1)+7(20-\bar{1})+\sqrt{6}(21-\bar{2})$$
$$+\ 2\sqrt{6}(1\bar{1}-1)-4(\bar{2}0-1)-2\sqrt{6}(\bar{2}1-2)+\sqrt{6}(2\bar{1}-2)-7(0-\bar{1}-2)$$
$$-\ 14(0-1-\bar{2})-7\sqrt{6}(1-2-\bar{2})+21(\bar{0}-1-2))/4\sqrt{70}$$

$$(15) = (-15(2\bar{2}1)+2\sqrt{6}(0-\bar{1}-2)-\sqrt{6}(0-1-\bar{2})-(21-\bar{2})$$
$$-\ \sqrt{6}(\bar{0}-1-2)-3(1-2-\bar{2})+8(1\bar{1}-1)-6(10\bar{0})+3\sqrt{6}(2\bar{0}-1)-2\sqrt{6}(20-\bar{1})$$
$$+\ 4(2\bar{1}-2)-\sqrt{6}(\bar{2}0-1)-2(\bar{2}1-2))/4\sqrt{30}$$

$$(16) = (-(\bar{2}\bar{1}-1)-2(2\bar{2}-\bar{2})+\sqrt{6}(1\bar{1}\bar{0})+(\bar{2}1-\bar{1})$$
$$-\ \sqrt{6}(\bar{0}-1-\bar{1})-(1-\bar{1}-\bar{2})+2(\bar{2}-2-\bar{2})+(\bar{1}-1-\bar{2}))/2\sqrt{6}$$

$$(17) = (-\sqrt{6}(1\bar{1}\bar{0})+3(\bar{2}0\bar{0})+3(\bar{2}1-\bar{1})$$
$$-\ (\bar{2}\bar{1}-1)-2(2\bar{1}-\bar{1})-(2\bar{2}-\bar{2})+\sqrt{6}(\bar{0}-1-\bar{1})-3(0\bar{0}-\bar{2})+3(\bar{1}-1-\bar{2})$$
$$-\ 2(\bar{1}-\bar{1}-2)-(1-\bar{1}-\bar{2})+(\bar{2}-2-\bar{2}))/\sqrt{60}$$

TABLE 28--Continued

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(18) = $i(12(\bar{2}0\bar{0})+12(2\bar{1}-\bar{1})+(1\bar{1}\bar{0})-9(\bar{2}\bar{1}-1)$

$- 3(\bar{2}1-\bar{1})+6(2\bar{2}-\bar{2})-\sqrt{6}(\bar{0}-1-\bar{1})-3(\bar{1}-1-\bar{2})-9(1-\bar{1}-\bar{2})-6(\bar{2}-2-\bar{2})$

$- 12(0\bar{0}-\bar{2})+12(\bar{1}-\bar{1}-2))/\sqrt{840}$

(19) = $i((\bar{2}\bar{1}-1)+(\bar{2}0\bar{0})-(2\bar{2}-\bar{2})-(\bar{2}1-\bar{1})$

$- (\bar{1}-1-\bar{2})-(0\bar{0}-\bar{2})+(\bar{2}-2-\bar{2})+(1-\bar{1}-\bar{2}))/\sqrt{8}$

(20) = $i(4(2\bar{1}-\bar{1})-5(2\bar{2}-\bar{2})-3(\bar{2}\bar{1}-1)-(\bar{2}1-\bar{1})$

$- 3(\bar{2}0\bar{0})-2\sqrt{6}(1\bar{1}\bar{0})-(\bar{1}-1-\bar{2})-3(1-\bar{1}-\bar{2})+5(\bar{2}-2-\bar{2})$

$+ 3(0\bar{0}-\bar{2})+4(\bar{1}-\bar{1}-2)+2\sqrt{6}(\bar{0}-1-\bar{1}))/2\sqrt{42}$

(21) = $(2(10-1)-(20-2))/\sqrt{5}$

(22) = $((10-1)+2(20-2)/\sqrt{5}$

(23) = $i((\bar{1}-\bar{1}-2)+(\bar{1}-\bar{1}-2)+(1-\bar{1}-\bar{2})-(\bar{2}\bar{1}-1)$

$- (\bar{2}1-\bar{1})-(2\bar{1}-\bar{1}))/\sqrt{6}$

(24) = $(-(\bar{1}-\bar{1}-2)-(\bar{1}-1-\bar{2})-(1-\bar{1}-\bar{2})-(\bar{2}\bar{1}-1)$

$- (\bar{2}1-\bar{1})-(2\bar{1}-\bar{1}))/\sqrt{6}$

(25) = $(-2(20-\bar{1})-2(2\bar{0}-1)-2(\bar{2}0-1)+\sqrt{6}(21-\bar{2})$

$+ \sqrt{6}(2\bar{1}-2)+\sqrt{6}(\bar{2}1-2))/\sqrt{30}$

(26) = $(2(\bar{1}\bar{0}-\bar{2})-\sqrt{6}(\bar{2}-\bar{1}-\bar{2}))/\sqrt{10}$

(27) = $(3(20-\bar{1})+3(2\bar{0}-1)+3(\bar{2}0-1)$

$+ \sqrt{6}(21-\bar{2})+\sqrt{6}(2\bar{1}-2)+\sqrt{6}(\bar{2}1-2)+5(0-\bar{1}-2)+5(\bar{0}-1-2)+5(0-1-\bar{2}))/2\sqrt{30}$

(28) = $(-3(\bar{1}\bar{0}-\bar{2})-\sqrt{6}(\bar{2}-\bar{1}-\bar{2})-5(\bar{2}\bar{1}\bar{0}))/\sqrt{40}$

(29) = $-(3(\bar{2}0-1)+3(2\bar{0}-1)+3(20-\bar{1})+\sqrt{6}(\bar{2}1-2)$

$+ \sqrt{6}(2\bar{1}-2)+\sqrt{6}(21-\bar{2})-3(\bar{0}-1-2)-3(0-\bar{1}-2)-3(0-1-\bar{2}))/6\sqrt{2}$

(30) = $(3(\bar{1}\bar{0}-\bar{2})+\sqrt{6}(\bar{2}-\bar{1}-\bar{2})-3(\bar{2}\bar{1}\bar{0}))/2\sqrt{6}$

$$H' = \left(\frac{1}{2\mu^2C^2}\right)\left[\left(\frac{1}{r}\right)\frac{\partial U(r)}{\partial r}\right]\vec{\ell}\cdot\vec{s} = \xi(r)\vec{\ell}\cdot\vec{s} \qquad (74)$$

where

μ is the reduced mass, i.e., $\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m}$,

C is the velocity of light

U(r) is the central field potential experienced by the electron, and

$\vec{\ell}$ and $\vec{s}$ are, respectively, the orbital and spin angular momentum of the electron.

Thus,

$$\xi(r) = \left(\frac{1}{2\mu^2C^2}\right)\left[\left(\frac{1}{r}\right)\frac{\partial U(r)}{\partial r}\right] \quad . \qquad (75)$$

The above description of the spin-orbit Hamiltonian is strictly valid only for the free ion case in which the central field, U(r), has spherical symmetry. Our assumption, after Ballahusen,[1] will be that we can use the free ion term, i.e., $\xi(r)\vec{\ell}\cdot\vec{s}$, to represent the spin-orbit interaction in the complex. Obviously, the symmetry of the complex is not spherical but, as Ballhausen pointed out,[2] the contribution to the total field made by the ligand field potential is not great and the assumption is largely justified.

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[1] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

[2] Ibid.

The single d electron matrix elements for the spin-orbit perturbation will have the following form

$$\hbar^2 \int_0^\infty R^*_{n,\ell}(r)R_{n,\ell}(r)\xi(r)r^2dr(1/\hbar^2)\cdot$$

$$<(n,\ell,m_\ell,m_s)|\vec{\ell}\cdot\vec{s}|(n,\ell,m_\ell,m_s)> \qquad (76)$$

We define the radial part of (76) as the spin-orbit parameter zeta (ζ). That is

$$\zeta = \hbar^2 \int_0^\infty R^*_{n,\ell}(r)R_{n,\ell}(r)\xi(r)r^2dr\ . \qquad (77)$$

The many electron matrix elements (H'_{jk}) are then given by

$$H'_{jk} = (\zeta/\hbar^2)<\psi_j|\sum_i \vec{\ell}_i\cdot\vec{s}_i|\psi_k>\ . \qquad (78a)$$

Hence, for d^3 we have

$$H'_{jk} = (\zeta/\hbar^2)<\psi_j|\sum_{i=1}^{3} \vec{\ell}_i\cdot\vec{s}_i|\psi_k>\ . \qquad (78b)$$

The complete form of the anuglar momentum operator $\vec{\ell}\cdot\vec{s}$ is

$$\vec{\ell}\cdot\vec{s} = \vec{\ell}_x\cdot\vec{s}_x + \vec{\ell}_y\cdot\vec{s}_y + \vec{\ell}_z\cdot\vec{s}_z \qquad (79)$$

Letting

$$\vec{\ell}_\pm = \vec{\ell}_x \pm i\,\vec{\ell}_y \quad \text{and} \qquad (80a)$$

$$\vec{s}_\pm = \vec{s}_x \pm i\,\vec{s}_y \qquad (80b)$$

we find that

$$\vec{\ell}_x \cdot \vec{s}_x + \vec{\ell}_y \cdot \vec{s}_y = (\vec{\ell}_+ \cdot \vec{s}_- + \vec{\ell}_- \cdot \vec{s}_+)/2 \ . \tag{81}$$

Hence,

$$\vec{\ell} \cdot \vec{s} = \vec{\ell}_z \cdot \vec{s}_z + (\vec{\ell}_+ \cdot \vec{s}_- + \vec{\ell}_- \cdot \vec{s}_+)/2 \ . \tag{82}$$

In spherical polar coordinates the z component of the angular momentum is $i\hbar(\frac{\partial}{\partial\phi})$. Application of $i\hbar(\frac{\partial}{\partial\phi})$ to the ϕ dependent part of the wave function yields for ℓ_z

$$\vec{\ell}_z \, e^{im_\ell\phi} = \hbar m_\ell \, e^{im_\ell\phi} \tag{82a}$$

and for $\vec{s}_z$

$$\vec{s}_z \, e^{im_s\phi} = \hbar m_s \, e^{im_s\phi} \ . \tag{82b}$$

In simplified microstate notation we have

$$\vec{\ell}_z(m_\ell) = \hbar m_\ell (m_\ell) \qquad \text{and} \tag{83a}$$

$$\vec{s}_z(m_s) = \hbar m_s (m_s) \ .$$

On combining the two we have

$$\vec{\ell}_z \cdot \vec{s}_z (m_\ell, m_s) = \hbar^2 m_\ell m_s (m_\ell, m_s) \ . \tag{84}$$

To illustrate the use of the operator $\vec{\ell}_z \cdot \vec{s}_z$ let us apply this operator to the microstate $(2\bar{1}0)$. Thus, we have

$$(1/\hbar^2)\ \sum_{i=1} (\vec{\ell}_z \cdot \vec{s}_z)_i (2\bar{1}0) =$$

$$(2)(1/2)(2\bar{1}0) + (1)(-1/2)(2\bar{1}0)$$

$$+\ (0)(1/2)(2\bar{1}0) = (1/2)(2\bar{1}0)\ .$$

For d electrons m_ℓ may take on values of ±2, ±1 and 0. Application of the orbital angular momentum raising and lowering operators, (cf. eqns. 9a and 9b), to the single electron functions will yield the results given in Table 29.

TABLE 29

The Evaluation of $\ell_\pm(m_\ell)$ for $m_\ell \le 2$

$\ell_+(m_\ell)$	$\ell_-(m_\ell)$
$\ell_+(+2) = 0$	$\ell_-(+2) = 2\hbar(+1)$
$\ell_+(+1) = 2\hbar(+2)$	$\ell_-(+1) = \sqrt{6}\,\hbar(0)$
$\ell_+(0) = \sqrt{6}\,\hbar(+1)$	$\ell_-(0) = \sqrt{6}\,\hbar(-1)$
$\ell_+(-1) = \sqrt{6}\,\hbar(0)$	$\ell_-(-1) = 2\hbar(-2)$
$\ell_+(-2) = 2\hbar(-1)$	$\ell_-(-2) = 0$

While for $\vec{s}_\pm$, (cf. eqns. 9c and 9d), with $m_s = \pm 1/2$ we obtain

$$\vec{s}_+(\alpha) = 0 \tag{85a}$$

$$\vec{s}_+(\beta) = \hbar(\alpha) \tag{85b}$$

$$\vec{s}_-(\alpha) = \hbar(\beta) \tag{85c}$$

$$\vec{s}_-(\beta) = 0 \tag{85d}$$

Thus, using (82) as developed we can calculate the spin-orbit matrix elements, (78b), for Γ_6^Q and Γ_7^Q as multiples of the parameter zeta (ζ). The non-zero spin-orbit matrix elements are given in Table 30. To obtain the complete energy matrices for the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme we need only properly superimpose the tetragonal matrices given in Table 20, which contain the parameters of the first three perturbations, onto the 30 x 30 Γ_6^Q and Γ_7^Q matrices garnered from Table 30.

The $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme

In the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme that we have presented the spin-orbit interaction has been included as the last perturbation. If the spin-orbit interaction becomes more important than the axial ligand field potential then the coupling scheme with the perturbations in the following sequence will result.

$$e^2/r_{ij}, \text{ then } V_c, \text{ then } \xi(r)\ell\cdot s, \text{ then } V_a$$

This is the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme.

The Cubic Ligand Field

The first half of the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme is identical to that of the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme. Hence, we need not repeat the calculations for the cubic perturbation, the

TABLE 30

The Non-Zero Matrix Elements $(H'_{jk}\text{'s})$ for the Spin-Orbit Perturbation of the $\{L,S,X^C,X^Q,\Gamma^Q\}$ Coupling Scheme

The number of the eigenvectors (the j's and k's below) is consistent with Table 28a.

Γ_6^Q

i	j	ζ	i	j	ζ
1	6	$7/\sqrt{210}$	2	12	$-i\sqrt{14}/4$
1	7	$3/\sqrt{15}$	2	13	$-i\sqrt{6}/12$
1	11	$7/\sqrt{420}$	2	14	$1/\sqrt{70}$
1	12	$i\sqrt{6}/4$	2	15	$-1/\sqrt{42}$
1	13	$-i\sqrt{14}/4$	2	22	$5/\sqrt{35}$
1	14	$\sqrt{30}/10$	2	27	$\sqrt{70}/28$
1	15	$-1/\sqrt{2}$	2	28	$i\sqrt{210}/28$
1	21	$4/\sqrt{15}$	2	29	$-5/2\sqrt{42}$
1	22	$-3/\sqrt{15}$	2	30	$-5i/\sqrt{56}$
1	25	$2/\sqrt{30}$	3	7	$-\sqrt{5}/6$
1	26	$2i/\sqrt{10}$	3	8	$-3i/\sqrt{60}$
1	27	$-\sqrt{30}/20$	3	9	$-\sqrt{14}/6$
1	28	$-3i/\sqrt{40}$	3	10	$-1/\sqrt{10}$
1	29	$1/\sqrt{8}$	3	14	$\sqrt{10}/6$
1	30	$i\sqrt{6}/4$	3	16	$3i/\sqrt{30}$
2	6	$-3/\sqrt{10}$	3	19	$\sqrt{7}/3$
2	7	$1/\sqrt{35}$	3	20	$1/\sqrt{5}$
2	11	$-3/2\sqrt{5}$	3	22	$\sqrt{5}/3$

TABLE 30--Continued

i	j	ζ	i	j	ζ
3	27	$-\sqrt{10}/6$	5	20	$i\sqrt{2}/5$
3	28	$-5i/\sqrt{30}$	6	11	$\sqrt{2}/3$
4	7	$-5/6\sqrt{7}$	6	12	$-i\sqrt{35}/10$
4	8	$i\sqrt{21}/10$	6	13	$9i/\sqrt{60}$
4	9	$-\sqrt{10}/6$	6	25	$\sqrt{7}/3$
4	10	$\sqrt{14}/10$	6	26	$-7i/\sqrt{21}$
4	14	$-5/6\sqrt{14}$	7	12	$2i/\sqrt{10}$
4	15	$-\sqrt{210}/28$	7	13	$2i/\sqrt{210}$
4	16	$i\sqrt{42}/20$	7	14	$1/4\sqrt{2}$
4	17	$-9i/10\sqrt{6}$	7	15	$-\sqrt{30}/24$
4	18	$-\sqrt{21}/5$	7	16	$5i/4\sqrt{6}$
4	19	$-\sqrt{5}/6$	7	17	$-5i/4\sqrt{42}$
4	20	$\sqrt{7}/10$	7	27	$1/4\sqrt{2}$
4	22	$5/3\sqrt{7}$	7	28	$-i\sqrt{6}/8$
4	27	$5/6\sqrt{14}$	7	29	$-\sqrt{30}/24$
4	28	$5i/2\sqrt{42}$	7	30	$i\sqrt{10}/8$
4	29	$\sqrt{210}/28$	8	14	$-5i/4\sqrt{6}$
4	30	$15i/2\sqrt{70}$	8	15	$-i\sqrt{10}/8$
5	8	$-\sqrt{6}/5$	8	16	$3\sqrt{2}/40$
5	10	$2i/5$	8	17	$3\sqrt{14}/40$
5	16	$-\sqrt{3}/5$	8	18	$4i/5$
5	17	$-\sqrt{21}/5$	8	19	$7i/\sqrt{105}$
5	18	$i\sqrt{6}/10$	8	20	$i\sqrt{3}/5$

TABLE 30--Continued

i	j	ζ	i	j	ζ
8	27	$5i/4\sqrt{6}$	12	21	$-2i/\sqrt{10}$
8	28	$5\sqrt{2}/8$	12	22	$-i/\sqrt{10}$
8	29	$i\sqrt{10}/8$	12	23	$-1/\sqrt{2}$
8	30	$\sqrt{30}/8$	12	24	$i/\sqrt{2}$
9	16	$-7i/\sqrt{105}$	12	25	$-2i/\sqrt{5}$
9	17	$i/\sqrt{15}$	12	27	$-i/\sqrt{5}$
9	18	$-\sqrt{210}/40$	12	29	$i/\sqrt{3}$
9	19	$3\sqrt{2}/16$	13	13	$1/12$
9	20	$3\sqrt{70}/80$	13	14	$-i/\sqrt{105}$
10	16	$-i\sqrt{3}/5$	13	15	$i/3\sqrt{7}$
10	17	$-i\sqrt{21}/5$	13	22	$5i/\sqrt{210}$
10	18	$\sqrt{6}/40$	13	23	$5/\sqrt{42}$
10	19	$21/8\sqrt{70}$	13	24	$-5i/\sqrt{42}$
10	20	$-11/40\sqrt{2}$	13	27	$5i/\sqrt{105}$
11	11	$-1/3$	13	29	$-5i/3\sqrt{7}$
11	12	$-i\sqrt{70}/20$	14	14	$-1/8$
11	13	$9i/2\sqrt{30}$	14	15	$-\sqrt{15}/24$
11	21	$-\sqrt{7}/3$	14	16	$-5i/8\sqrt{3}$
11	25	$\sqrt{14}/3$	14	17	$-5i/8\sqrt{21}$
12	12	$-1/4$	14	22	$-1/4\sqrt{2}$
12	13	$\sqrt{21}/12$	14	24	$-\sqrt{10}/8$
12	14	$-i/\sqrt{5}$	14	27	$1/4$
12	15	$i/\sqrt{3}$	14	29	$\sqrt{15}/12$

TABLE 30--Continued

i	j	ζ	i	j	ζ
15	15	$-1/24$	17	27	$5i/4\sqrt{21}$
15	16	$i\sqrt{5}/8$	17	29	$15i/4\sqrt{35}$
15	17	$-15i/8\sqrt{35}$	18	18	$-1/4$
15	22	$\sqrt{30}/24$	18	19	$-\sqrt{105}/40$
15	23	$i/\sqrt{6}$	18	20	$\sqrt{3}/40$
15	24	$1/4\sqrt{6}$	19	19	$-3/16$
15	27	$\sqrt{15}/12$	19	20	$-21/16\sqrt{35}$
15	29	$1/12$	20	20	$11/80$
16	16	$-3/40$	21	25	$\sqrt{2}/3$
16	17	$3\sqrt{7}/40$	21	26	$i/\sqrt{6}$
16	18	$i\sqrt{8}/5$	22	27	$-1/\sqrt{2}$
16	19	$-7i/\sqrt{210}$	22	28	$-i\sqrt{6}/4$
16	20	$-i\sqrt{6}/10$	22	29	$5/\sqrt{30}$
16	22	$-5i/4\sqrt{6}$	22	30	$i\sqrt{10}/4$
16	24	$i\sqrt{30}/8$	23	24	i
16	27	$5i/4\sqrt{3}$	23	29	$2i/\sqrt{6}$
16	29	$-i\sqrt{5}/4$	24	27	$\sqrt{10}/4$
17	17	$3/8$	24	29	$-1/2\sqrt{6}$
17	19	$-i/\sqrt{30}$	25	25	$-1/6$
17	20	$i\sqrt{42}/10$	26	26	$-1/2$
17	22	$5i/4\sqrt{42}$	27	27	$1/4$
17	23	$15/\sqrt{210}$	27	29	$\sqrt{15}/12$
17	24	$45i/4\sqrt{210}$	28	28	$3/4$

TABLE 30--Continued

i	j	ζ	i	j	ζ
28	30	$\sqrt{15}/4$	30	30	$1/4$
29	29	$1/12$			
		Γ_7^Q			
1	6	$-\sqrt{35}/10$	2	13	$-1/3\sqrt{14}$
1	7	$-3/\sqrt{10}$	2	16	$-1/3\sqrt{7}$
1	11	$i/\sqrt{8}$	2	19	$-i\sqrt{21}/6$
1	12	$-i\sqrt{42}/12$	2	20	$-i/6$
1	13	$-1/\sqrt{6}$	2	24	$5/3\sqrt{7}$
1	16	$-1/\sqrt{3}$	2	27	$\sqrt{210}/28$
1	19	$i/2$	2	28	$-15/2\sqrt{70}$
1	20	$-i\sqrt{21}/6$	2	29	$5/6\sqrt{14}$
1	24	$-1/\sqrt{3}$	2	30	$-5/2\sqrt{42}$
1	25	$2/\sqrt{10}$	3	11	$2/\sqrt{6}$
1	26	$-6/\sqrt{30}$	3	12	$2/3\sqrt{14}$
1	27	$-3/\sqrt{40}$	3	13	$-i\sqrt{2}/6$
1	28	$3\sqrt{30}/20$	3	14	$-5/\sqrt{70}$
1	29	$-1/2\sqrt{6}$	3	16	$i/6$
1	30	$\sqrt{2}/4$	3	18	$\sqrt{35}/14$
2	6	$9/\sqrt{60}$	3	19	$-1/\sqrt{3}$
2	7	$-3/\sqrt{210}$	3	20	$-1/3\sqrt{7}$
2	11	$-i\sqrt{42}/12$	3	24	$-i/3$
2	12	$-i/6\sqrt{2}$	3	29	$i\sqrt{2}/6$

TABLE 30--Continued

i	j	ζ	i	j	ζ
3	30	-i/√6	6	11	i√70/20
4	7	5/2√42	6	12	-9i/2√30
4	8	-3i√14/20	6	19	i√35/10
4	9	√15/6	6	20	-9i/√60
4	10	-√21/10	6	21	√21/3
4	13	-√70/28	6	25	√14/3
4	14	-3i√2/20	7	7	1/8
4	15	-√7/5	7	8	5i/8√3
4	16	-√35/14	7	11	-i/√5
4	17	-√14/5	7	12	-i/√105
4	18	-3i/10	7	13	√15/24
4	24	-5/√35	7	14	5i/8√21
4	27	5/2√42	7	16	√30/24
4	28	-5/2√14	7	18	5i/4√42
4	29	-√70/28	7	19	-2i/√10
4	30	√210/28	7	20	-2i/√210
5	8	3/5	7	22	√6/8
5	10	-i√6/5	7	24	√30/24
5	14	-√7/5	7	27	1/4
5	15	i/5√2	7	29	√15/12
5	17	i/5	8	8	3/40
5	18	-√14/5	8	9	7i/√210
6	6	1/3	8	10	i√6/10

TABLE 30--Continued

i	j	ζ	i	j	ζ
8	13	$i\sqrt{5}/8$	11	13	$-i/\sqrt{3}$
8	14	$-3\sqrt{7}/40$	11	16	$2i/\sqrt{6}$
8	15	$-i\sqrt{8}/5$	11	19	$-1/\sqrt{8}$
8	16	$i\sqrt{10}/8$	11	20	$\sqrt{42}/12$
8	17	$-4i/5$	11	21	$6i/\sqrt{30}$
8	18	$-3\sqrt{14}/40$	11	22	$3i/\sqrt{30}$
8	22	$5i/4\sqrt{2}$	11	23	$1/\sqrt{6}$
8	24	$-\sqrt{10}/8$	11	24	$-i/\sqrt{6}$
8	27	$5i/4\sqrt{3}$	11	25	$-2i/\sqrt{5}$
8	29	$-i\sqrt{5}/4$	11	27	$-i/\sqrt{5}$
9	9	$3/16$	11	29	$i/\sqrt{3}$
9	10	$21/16\sqrt{35}$	12	12	$-1/12$
9	14	$i/\sqrt{30}$	12	13	$-i/3\sqrt{7}$
9	15	$\sqrt{105}/40$	12	16	$i\sqrt{14}/21$
9	17	$\sqrt{210}/40$	12	19	$\sqrt{42}/12$
9	18	$-i/\sqrt{15}$	12	20	$1/6\sqrt{2}$
10	10	$-11/80$	12	22	$-5i/\sqrt{70}$
10	14	$i\sqrt{42}/10$	12	23	$-5/3\sqrt{14}$
10	15	$-\sqrt{3}/40$	12	24	$5i/3\sqrt{14}$
10	17	$-\sqrt{6}/40$	12	27	$5i/\sqrt{105}$
10	18	$i\sqrt{21}/5$	12	29	$-5i/3\sqrt{7}$
11	11	$1/4$	13	13	$1/24$
11	12	$-\sqrt{21}/12$	13	14	$15i/8\sqrt{35}$

TABLE 30--Continued

i	j	ζ	i	j	ζ
13	16	$-\sqrt{2}/24$	16	30	$1/4\sqrt{6}$
13	18	$-15i/4\sqrt{70}$	18	23	$-\sqrt{35}/7$
13	19	$-2i/\sqrt{6}$	18	27	$-5i/4\sqrt{42}$
13	20	$-i\sqrt{14}/21$	18	28	$-5i/4\sqrt{14}$
13	22	$-5/4\sqrt{10}$	18	29	$15i/4\sqrt{70}$
13	23	$-i\sqrt{2}/6$	18	30	$3i\sqrt{210}/56$
13	24	$-\sqrt{2}/24$	19	23	$1/\sqrt{3}$
13	27	$\sqrt{15}/12$	19	25	$2i/\sqrt{10}$
13	29	$1/12$	19	26	$6i/\sqrt{30}$
14	14	$-3/8$	19	27	$i/\sqrt{10}$
14	16	$15i/4\sqrt{70}$	19	28	$3i/\sqrt{30}$
14	18	$3\sqrt{2}/8$	19	29	$i/\sqrt{6}$
14	22	$-5i/4\sqrt{14}$	19	30	$i/\sqrt{2}$
14	23	$-5/\sqrt{70}$	20	23	$-5/3\sqrt{7}$
14	24	$-15i/4\sqrt{70}$	20	27	$-5i/\sqrt{210}$
14	27	$5i/4\sqrt{21}$	20	28	$-5i/\sqrt{70}$
14	29	$15i/4\sqrt{35}$	20	29	$-5i/3\sqrt{14}$
15	15	$1/4$	20	30	$-5i/\sqrt{42}$
15	17	$-1/\sqrt{8}$	21	25	$-1/\sqrt{6}$
16	23	$-i/3$	22	27	$\sqrt{6}/4$
16	27	$-\sqrt{30}/24$	22	29	$-\sqrt{10}/4$
16	28	$-\sqrt{10}/8$	23	24	$i/6$
16	29	$\sqrt{2}/24$	23	29	$-i\sqrt{8}/3$

TABLE 30--Continued

i	j	ζ	i	j	ζ
23	30	$-2i/\sqrt{6}$	27	27	$-1/4$
24	27	$-5/\sqrt{30}$	27	29	$-\sqrt{15}/12$
24	28	$\sqrt{10}/4$	28	28	$-3/4$
24	29	$\sqrt{2}/6$	28	30	$-\sqrt{15}/4$
24	30	$-1/2\sqrt{6}$	29	29	$-1/12$
25	25	$1/6$	30	30	$-1/4$
26	26	$1/2$			

cubic wave functions and the corresponding energy matrices being the same as in the $\{L,S,X^C,X^Q,\Gamma^Q\}$ scheme (cf. Tables 17 and 19).

The Spin-Orbit Interaction

In this coupling scheme we spin-adopt the wave functions prior to considering the perturbation due to the axial ligand field. Therefore, the rotational double group of interest here is O'. The character table for O' is given in Table 31a. In Table 31b the characters for the representations generated by the doublet (J=1/2) spin state and the quartet (J=3/2) spin state are given.

By inspection of Table 31 we see that the doublet spin state transforms as Γ_6 and the quartet spin state as Γ_8.

The decomposition of the direct products of space and spin is given in Table 32. This result tells us how the cubic levels are split when the spin-orbit perturbation is added.

In Table 33a the basis functions we have chosen for the individual components of $\Gamma_6{}^C$, $\Gamma_7{}^C$ and $\Gamma_8{}^C$ are given. Also, in Table 33a the transformation properties of the various components of $\Gamma_6{}^C$, $\Gamma_7{}^C$ and $\Gamma_8{}^C$ for the rotations $C_4(z)$, $C_2{}'(y)$ and $C_3(z')$ of O' are given. Note that for $\Gamma_8{}^C$ the basis functions are the quartet spin functions.

In Table 33b the various basis and the transformation properties for $C_4(z)$, $C_2{}'(y)$ and $C_3(z')$ of O' are given for the orbital representations.

In Table 34 the appropriate space and spin combinations which form the spin-adapted wave functions for the spin-orbit perturbation of this coupling scheme are given.

TABLE 31

a) The Character Table for O'

	E	R	$4C_3$ $4C_3^2R$	$4C_3^2$ $4C_3R$	$3C_2$ $3C_2R$	$3C_4$ $3C_4^3R$	$3C_4^3$ $3C_4R$	$6C_2'$ $6C_2'R$
$\Gamma_1(A_1)$	1	1	1	1	1	1	1	1
$\Gamma_2(A_2)$	1	1	1	1	1	-1	-1	-1
$\Gamma_3(E)$	2	2	-1	-1	2	0	0	0
$\Gamma_4(T_1)$	3	3	0	0	-1	1	1	-1
$\Gamma_5(T_2)$	3	3	0	0	-1	-1	-1	1
Γ_6	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	2	-2	1	-1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	4	-4	-1	1	0	0	0	0

b) Representations of the Doublet (J=1/2) and Quartet (J=3/2) Spin States of d^3 in O'

J=1/2	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0
J=3/2	4	-4	-1	1	0	0	0	0

TABLE 32

The Decomposition of the Cubic Levels of the $\{L,S,\chi^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme When the Spin-Orbit Perturbation is Added

Cubic Level	Direct[k] Product	Spin-Orbit Level(s)
$^2A_{1g}$	$a_1 \times \Gamma_6$	Γ_6
$^2A_{2g}$	$a_2 \times \Gamma_6$	Γ_7
^2E_g	$e \times \Gamma_6$	Γ_8
$^2T_{1g}$	$t_1 \times \Gamma_6$	$\Gamma_6 + \Gamma_8$
$^2T_{2g}$	$t_2 \times \Gamma_6$	$\Gamma_7 + \Gamma_8$
$^4A_{2g}$	$a_2 \times \Gamma_8$	Γ_8
$^4T_{1g}$	$t_1 \times \Gamma_8$	$\Gamma_6 + \Gamma_7 + 2\Gamma_8$
$^4T_{2g}$	$t_2 \times \Gamma_8$	$\Gamma_6 + \Gamma_7 + 2\Gamma_8$

[k] In the direct product the orbital part of the wave function is given lower case notation (i.e., a_1, a_2, e, t_1 and t_2) while the spin part of the wave function is given gamma notation (i.e., Γ_6, Γ_7 and Γ_8).

TABLE 33

a) The Basis Functions and the Transformation Properties (for $C_4(z)$, $C_2^{'}(y)$ and $C_3(z'))$ of $\Gamma_{6a,b}$, $\Gamma_{7a,b}$, and $\Gamma_{8a,b,c,d}$ of O'

Representation	Basis[k]	$C_4(z)$	$C_2^{'}(y)$	$C_3(z^{'})$
Γ_{6a}	α	$e^{i\pi/4}\Gamma_{6a}$	Γ_{6b}	$e^{i\pi/4}(\Gamma_{6a}+i\Gamma_{6b})/\sqrt{2}$
Γ_{6b}	β	$e^{-i\pi/4}\Gamma_{6b}$	$-\Gamma_{6a}$	$e^{-i\pi/4}(i\Gamma_{6a}+\Gamma_{6b})/\sqrt{2}$
Γ_{7a}	—	$e^{3i\pi/4}\Gamma_{7a}$	Γ_{7b}	—
Γ_{7b}	—	$e^{-3i\pi/4}\Gamma_{7b}$	$-\Gamma_{7a}$	—
Γ_{8a}	$(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)/\sqrt{3}$	$e^{i\pi/4}\Gamma_{8a}$	$-\Gamma_{8b}$	$e^{i\pi/4}(-\Gamma_{8a}+i\Gamma_{8b}+\sqrt{3}\Gamma_{8c}-\sqrt{3}\Gamma_{8d})/\sqrt{8}$
Γ_{8b}	$(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	$e^{-i\pi/4}\Gamma_{8b}$	Γ_{8a}	$e^{-i\pi/4}(i\Gamma_{8a}-\Gamma_{8b}-\sqrt{3}\Gamma_{8c}+i\sqrt{3}\Gamma_{8d})/\sqrt{8}$
Γ_{8c}	$\alpha\alpha\alpha$	$e^{3i\pi/4}\Gamma_{8c}$	Γ_{8d}	$e^{3i\pi/4}(i\sqrt{3}\Gamma_{8a}-\sqrt{3}\Gamma_{8b}+\Gamma_{8c}-i\Gamma_{8d})/\sqrt{8}$

TABLE 33--Continued

Representation	Basis[k]	$C_4(z)$	$C_2'(y)$	$C_3(z')$
Γ_{8d}	$\beta\beta\beta$	$e^{-3i\pi/4}\Gamma_{8d}$	$-\Gamma_{8c}$	$e^{-3i\pi/4}(-\sqrt{3}\Gamma_{8a}$ $+i\sqrt{3}\Gamma_{8b}-i\Gamma_{8c}$ $+\Gamma_{8d})/\sqrt{8}$

[k] No basis is given for Γ_7. Nonetheless the transformation properties of Γ_{7a} and Γ_{7b} must be the same as Γ_{8c} and Γ_{8d}, respectively, for $C_4(z)$ and $C_2'(y)$. This is so because both $\Gamma_{7a,b}$ and $\Gamma_{8c,d}$ transform as $\Gamma_{7a,b}$ when the symmetry is lowered to D_4'.

TABLE 33--Continued

b) The Basis Functions and the Transformation Properties (for $C_4(z)$, $C_2'(y)$ and $C_3(z')$) of Γ_1 Through Γ_5 of O'

Representation	Basis	$C_4(z)$	$C_2'(y)$	$C_3(z')$
$\Gamma_1(a_1)$	s	a_1	a_1	a_1
$\Gamma_2(a_2)$	——	$-a_2$	a_2	a_2
$\Gamma_{3a}(e_a)$	$(a^2-x^2-y^2)$	e_a	e_a	$-(e_a+\sqrt{3}e_b)/2$
$\Gamma_{3b}(e_b)$	(x^2-y^2)	$-e_b$	e_b	$(\sqrt{3}e_a-e_b)/2$
$\Gamma_{4a}(t_{1a})$	z	t_{1a}	$-t_{1a}$	t_{1b}
$\Gamma_{4b}(t_{1b})$	y	t_{1c}	t_{1b}	t_{1c}
$\Gamma_{4c}(t_{1c})$	x	$-t_{1b}$	$-t_{1c}$	t_{1a}
$\Gamma_{5a}(t_{2a})$	xy	$-t_{2a}$	$-t_{2a}$	t_{2b}
$\Gamma_{5b}(t_{2b})$	xz	$-t_{2c}$	t_{2b}	t_{2c}
$\Gamma_{5c}(t_{2c})$	yz	t_{2b}	$-t_{2c}$	t_{2a}

TABLE 34

The Space and Spin Combinations^k Which Form the Wave Functions for the Spin-Orbit Perturbation of the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme

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$^2A^C_{1g}$

$\Gamma_{6a} = a_1 \Gamma_{6a}$

$\Gamma_{6b} = a_1 \Gamma_{6b}$

$^2A^C_{2g}$

$\Gamma_{7a} = a_2 \Gamma_{6b}$

$\Gamma_{7b} = -a_2 \Gamma_{6a}$

$^2E^C_g$

$\Gamma_{8a} = -e_a \Gamma_{6a}$

$\Gamma_{8b} = e_a \Gamma_{6b}$

$\Gamma_{8c} = e_b \Gamma_{6b}$

$\Gamma_{8d} = -e_b \Gamma_{6a}$

$^2T^C_{1g}$

$\Gamma_{6a} = (-t_{1a}\Gamma_{6a}-it_{1b}\Gamma_{6b}-t_{1c}\Gamma_{6b})/\sqrt{3}$

$\Gamma_{6b} = (t_{1a}\Gamma_{6b}+it_{1b}\Gamma_{6a}-t_{1c}\Gamma_{6a})/\sqrt{3}$

$\Gamma_{8a} = (-2t_{1a}\Gamma_{6a}+it_{1b}\Gamma_{6b}+t_{1c}\Gamma_{6b})/\sqrt{6}$

TABLE 34--Continued

$\Gamma_{8b} = (-2t_{1a}\Gamma_{6b}+it_{1b}\Gamma_{6a}-t_{1c}\Gamma_{6a})/\sqrt{6}$

$\Gamma_{8c} = (t_{1c}\Gamma_{6a}+it_{1b}\Gamma_{6a})/\sqrt{2}$

$\Gamma_{8d} = (-t_{1c}\Gamma_{6b}+it_{1b}\Gamma_{6b})/\sqrt{2}$

$^{2}T^{C}_{2g}$

$\Gamma_{7a} = (it_{1a}\Gamma_{6b}-t_{2b}\Gamma_{6a}-it_{2c}\Gamma_{6a})/\sqrt{3}$

$\Gamma_{7b} = (it_{2a}\Gamma_{6a}-t_{2b}\Gamma_{6b}+it_{2c}\Gamma_{6b})/\sqrt{3}$

$\Gamma_{8a} = -(t_{2b}\Gamma_{6b}+it_{2c}\Gamma_{6b})/\sqrt{2}$

$\Gamma_{8b} = (-t_{2b}\Gamma_{6a}+it_{2c}\Gamma_{6a})/\sqrt{2}$

$\Gamma_{8c} = (2it_{2a}\Gamma_{6b}+t_{2b}\Gamma_{6a}+it_{2c}\Gamma_{6a})/\sqrt{6}$

$\Gamma_{8d} = (2it_{2a}\Gamma_{6a}+t_{2b}\Gamma_{6b}-it_{2c}\Gamma_{6b})/\sqrt{6}$

$^{4}A^{C}_{2g}$

$\Gamma_{8a} = a_{2}\Gamma_{8d}$

$\Gamma_{8b} = a_{2}\Gamma_{8c}$

$\Gamma_{8c} = -a_{2}\Gamma_{8b}$

$\Gamma_{8d} = -a_{2}\Gamma_{8a}$

TABLE 34--Continued

$${}^4T^C_{1g}$$

$$\Gamma_{6a} = (-2it_{1a}\Gamma_{8a}+t_{1b}\Gamma_{8b}-it_{1c}\Gamma_{8b}+\sqrt{3}t_{1b}\Gamma_{8c}+i\sqrt{3}t_{1c}\Gamma_{8c})/2\sqrt{3}$$

$$\Gamma_{6b} = (2it_{1a}\Gamma_{8b}-t_{1b}\Gamma_{8a}-it_{1c}\Gamma_{8a}-\sqrt{3}t_{1b}\Gamma_{8d}+i\sqrt{3}t_{1c}\Gamma_{8d})/2\sqrt{3}$$

$$\Gamma_{7a} = (2it_{1a}\Gamma_{8c}-t_{1b}\Gamma_{8d}-it_{1c}\Gamma_{8d}+\sqrt{3}t_{1b}\Gamma_{8a}-i\sqrt{3}t_{1c}\Gamma_{8a})/2\sqrt{3}$$

$$\Gamma_{7b} = (2it_{1a}\Gamma_{8d}-t_{1b}\Gamma_{8c}+it_{1c}\Gamma_{8c}+\sqrt{3}t_{1b}\Gamma_{8b}+i\sqrt{3}t_{1c}\Gamma_{8b})/2\sqrt{3}$$

$$\Gamma_{8a}(1) = (it_{1a}\Gamma_{8a}+t_{1b}\Gamma_{8b}-it_{1c}\Gamma_{8b})/\sqrt{3}$$

$$\Gamma_{8b}(1) = -(it_{1a}\Gamma_{8b}+t_{1b}\Gamma_{8a}+it_{1c}\Gamma_{8a})/\sqrt{3}$$

$$\Gamma_{8c}(1) = (-it_{1a}\Gamma_{8c}-t_{1b}\Gamma_{8d}-it_{1c}\Gamma_{8d})/\sqrt{3}$$

$$\Gamma_{8d}(1) = (it_{1a}\Gamma_{8d}+t_{1b}\Gamma_{8c}-it_{1c}\Gamma_{8c})/\sqrt{3}$$

$$\Gamma_{8a}(2) = (2it_{1a}\Gamma_{8a}-t_{1b}\Gamma_{8b}+it_{1c}\Gamma_{8b}+\sqrt{3}t_{1b}\Gamma_{8c}+i\sqrt{3}t_{1c}\Gamma_{8c})/2\sqrt{3}$$

$$\Gamma_{8b}(2) = (-2it_{1a}\Gamma_{8b}+t_{1b}\Gamma_{8a}+it_{1c}\Gamma_{8a}-\sqrt{3}t_{1b}\Gamma_{8d}+i\sqrt{3}t_{1c}\Gamma_{8d})/2\sqrt{3}$$

$$\Gamma_{8c}(2) = (2it_{1a}\Gamma_{8c}-t_{1b}\Gamma_{8d}-it_{1c}\Gamma_{8d}-\sqrt{3}t_{1b}\Gamma_{8a}+i\sqrt{3}t_{1c}\Gamma_{8a})/2\sqrt{3}$$

$$\Gamma_{8d}(2) = (-2it_{1a}\Gamma_{8d}+t_{1b}\Gamma_{8c}-it_{1c}\Gamma_{8c}+\sqrt{3}t_{1b}\Gamma_{8b}+i\sqrt{3}t_{1c}\Gamma_{8b})/2\sqrt{3}$$

$${}^4T^C_{2g}$$

$$\Gamma_{6a} = (2t_{2a}\Gamma_{8d}+it_{2b}\Gamma_{8c}+t_{2c}\Gamma_{8c}-i\sqrt{3}t_{2b}\Gamma_{8b}+\sqrt{3}t_{2c}\Gamma_{8b})/2\sqrt{3}$$

$$\Gamma_{6b} = (-2t_{2a}\Gamma_{8c}-it_{2b}\Gamma_{8d}+t_{2c}\Gamma_{8d}+i\sqrt{3}t_{2b}\Gamma_{8a}+\sqrt{3}t_{2c}\Gamma_{8a})/2\sqrt{3}$$

$$\Gamma_{7a} = (-2t_{2a}\Gamma_{8b}-it_{2b}\Gamma_{8a}+t_{2c}\Gamma_{8a}-i\sqrt{3}t_{2b}\Gamma_{8d}-\sqrt{3}t_{2c}\Gamma_{8d})/2\sqrt{3}$$

$$\Gamma_{7b} = (2t_{2a}\Gamma_{8a}+it_{2b}\Gamma_{8b}+t_{2c}\Gamma_{8b}+i\sqrt{3}t_{2b}\Gamma_{8c}-\sqrt{3}t_{2c}\Gamma_{8d})/2\sqrt{3}$$

TABLE 34--Continued

$$\Gamma_{8a}(1) = (-t_{2a}\Gamma_{8d}+it_{2b}\Gamma_{8c}+t_{2c}\Gamma_{8c})/\sqrt{3}$$

$$\Gamma_{8b}(1) = (t_{2a}\Gamma_{8c}-it_{2b}\Gamma_{8d}+t_{2c}\Gamma_{8d})/\sqrt{3}$$

$$\Gamma_{8c}(1) = (-t_{2a}\Gamma_{8b}+it_{2b}\Gamma_{8a}-t_{2c}\Gamma_{8a})/\sqrt{3}$$

$$\Gamma_{8d}(1) = (t_{2a}\Gamma_{8a}-it_{2b}\Gamma_{8b}-t_{2c}\Gamma_{8b})/\sqrt{3}$$

$$\Gamma_{8a}(2) = (2t_{2a}\Gamma_{8d}+it_{2b}\Gamma_{8c}+t_{2c}\Gamma_{8c}+i\sqrt{3}t_{2b}\Gamma_{8b}-\sqrt{3}t_{2c}\Gamma_{8b})/2\sqrt{3}$$

$$\Gamma_{8b}(2) = (-2t_{2a}\Gamma_{8c}-it_{2b}\Gamma_{8d}+t_{2c}\Gamma_{8d}-i\sqrt{3}t_{2b}\Gamma_{8a}-\sqrt{3}t_{2c}\Gamma_{8a})/2\sqrt{3}$$

$$\Gamma_{8c}(2) = (-2t_{2a}\Gamma_{8b}-it_{2b}\Gamma_{8a}+t_{2c}\Gamma_{8a}+i\sqrt{3}t_{2b}\Gamma_{8d}+\sqrt{3}t_{2c}\Gamma_{8d})/2\sqrt{3}$$

$$\Gamma_{8d}(2) = (2t_{2a}\Gamma_{8a}+it_{2b}\Gamma_{8b}+t_{2c}\Gamma_{8b}-i\sqrt{3}t_{2b}\Gamma_{8c}+\sqrt{3}t_{2c}\Gamma_{8c})/2\sqrt{3}$$

---

[k] The orbital part of the wave function is given lower case notation (i.e., a_1, a_2, e, t_1 and t_2) while the spin part of the wave function is given gamma notation (i.e., Γ_6, Γ_7 and Γ_8).

The spin-orbit perturbation block diagonalizes the secular determinant into two 9 by 9's $(\Gamma_6$ and $\Gamma_7)$ and a 21 by 21 (Γ_8). This is illustrated in Fig. 9.

In Table 35 the spin-adapted wave functions in microstate form for the a components of Γ_6 and Γ_7 and for the a and c components of Γ_8 are given.

Lastly, the non-zero matrix elements for the spin-orbit perturbation of the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme are given in Table 36. These elements (the H'_{jk}'s) are calculated exactly as in the previous coupling scheme and are given as multiples of the spin-orbit parameter ζ.

To obtain the complete energy matrices to this point for the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme we need only appropriately superimpose the cubic matrices (given in Table 19) onto the spin-orbit matrices $(\Gamma_6{}^C$, $\Gamma_7{}^C$ and $\Gamma_8{}^C)$.

The Axial Ligand Field

The cubic states decompose as shown in Table 37 when the symmetry is lowered to $D_4'(D_{4h})$.

The tetragonal wave functions are then readily obtained from Table 35 and the matrix elements for the axial ligand field perturbation are calculated exactly as was done in the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme.

This last perturbation block diagonalizes the secular determinant into two 30 by 30's $(\Gamma_6{}^Q$ and $\Gamma_7{}^Q)$ as expected (cf. Fig. 8).

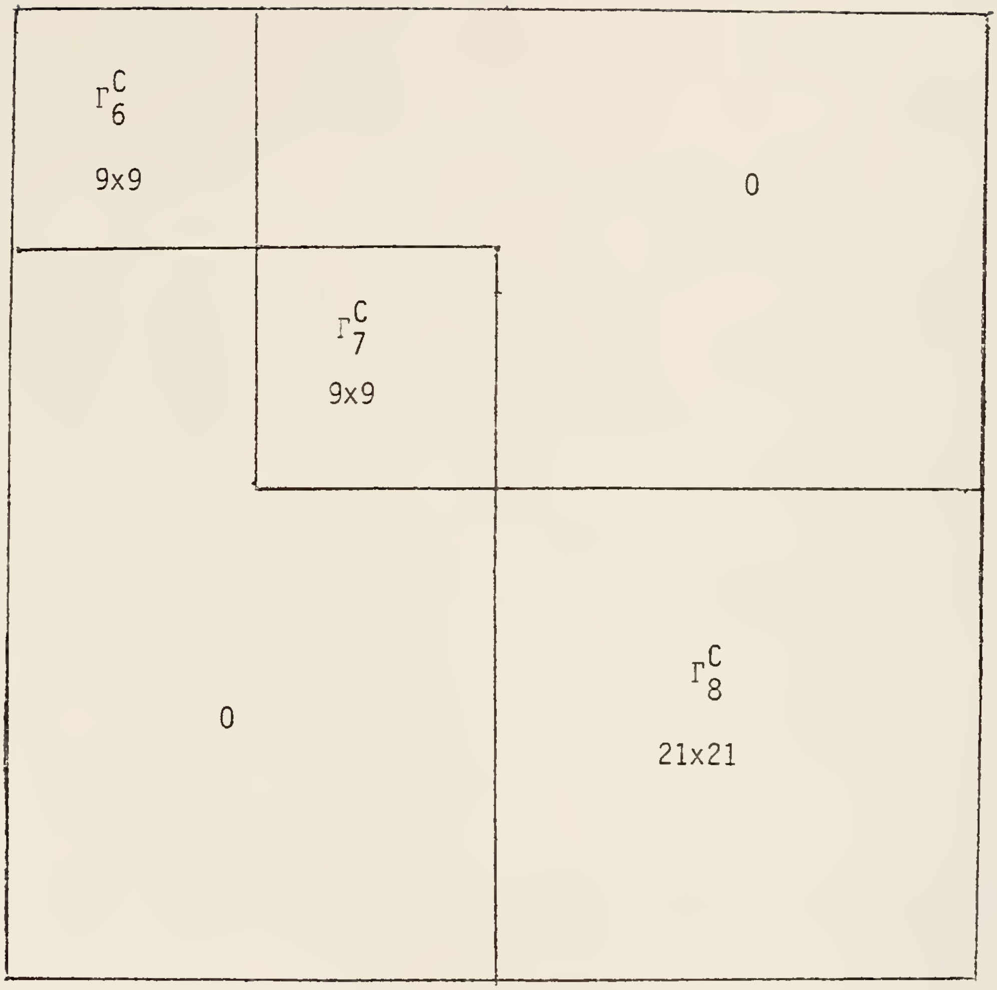

Figure 9. The Spin-Orbit Secular Determinant for d^3 for the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme.

TABLE 35

The Spin-Adapted Wave Functions in Microstate Form for the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme

Γ^C_{6a}

$$\begin{aligned}
{}^2A^C_{1g}({}^2G) = {} & [2(10\text{-}\bar{1})+\sqrt{6}(2\text{-}1\text{-}\bar{1})+2(20\text{-}\bar{2})-2(\bar{1}0\text{-}1)+\sqrt{6}(1\bar{1}\text{-}2)\\
& -2(\bar{2}0\text{-}2)+2(2\bar{2}\bar{0})+\sqrt{6}(21\bar{1})+\sqrt{6}(\text{-}1\text{-}\bar{1}\text{-}2)+2(0\text{-}2\text{-}\bar{2})]/4\sqrt{3}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{1g}({}^2P) = {} & [8(20\text{-}\bar{2})+6\sqrt{6}(1\bar{1}\text{-}2)-16(2\bar{0}\text{-}2)+8(\bar{2}0\text{-}2)\\
& +2(10\text{-}\bar{1})-6\sqrt{6}(2\text{-}1\text{-}\bar{1})-4(1\bar{0}\text{-}1)+2(\bar{1}0\text{-}1)-4\sqrt{6}(\bar{2}1\text{-}\bar{2})\\
& -4\sqrt{6}(2\bar{1}\text{-}\bar{2})+8\sqrt{6}(\bar{2}\bar{1}\text{-}2)+20(2\bar{0}\text{-}\bar{1})-16(\bar{2}\bar{0}\text{-}1)\\
& -4(\bar{2}0\text{-}\bar{1})-6\sqrt{6}(1\bar{1}\text{-}\bar{1})-6\sqrt{6}(\bar{1}0\bar{0})]/6\sqrt{70}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{1g}({}^2F) = {} & [-4(\bar{1}0\text{-}1)+8(1\bar{0}\text{-}1)-2\sqrt{6}(1\bar{1}\text{-}2)+2\sqrt{6}(2\text{-}1\text{-}\bar{1})-8(2\bar{0}\text{-}2)\\
& +4(\bar{2}0\text{-}2)-4(10\text{-}\bar{1})+4(20\text{-}\bar{2})+2\sqrt{6}(1\bar{1}\text{-}\bar{1})-3(\bar{2}\bar{0}\text{-}1)-\sqrt{6}(\bar{2}\bar{1}\text{-}2)\\
& -2\sqrt{6}(2\bar{1}\text{-}\bar{2})+3\sqrt{6}(\bar{2}1\text{-}\bar{2})-3\sqrt{6}(\bar{1}0\bar{0})+3(\bar{2}0\text{-}\bar{1})-5(\bar{0}\text{-}1\text{-}\bar{2})\\
& -5(0\text{-}\bar{1}\text{-}\bar{2})+10(\bar{0}\text{-}\bar{1}\text{-}2)+5\sqrt{6}(\bar{1}\text{-}2\text{-}\bar{2})]/12\sqrt{5}
\end{aligned}$$

$$\begin{aligned}
{}^2T^C_{1g}({}^2G) = {} & i[-4\sqrt{6}(\text{-}1\text{-}\bar{1}\text{-}2)-8(\text{-}0\text{-}2\text{-}\bar{2})+8(2\bar{2}0)+4\sqrt{6}(21\bar{1})\\
& +2\sqrt{6}(\bar{1}0\bar{0})-14(\bar{2}\bar{0}\text{-}1)+6(\bar{2}0\text{-}\bar{1})+8(2\bar{0}\text{-}\bar{1})+4\sqrt{6}(2\bar{1}\text{-}\bar{2})\\
& +4\sqrt{6}(1\bar{1}\text{-}\bar{1})-2\sqrt{6}(\bar{2}\bar{1}\text{-}2)-2\sqrt{6}(\bar{2}1\text{-}\bar{2})+6(0\text{-}\bar{1}\text{-}\bar{2})+2\sqrt{6}(\bar{1}\text{-}2\text{-}\bar{2})\\
& -4(\bar{0}\text{-}\bar{1}\text{-}2)-2(\bar{0}\text{-}1\text{-}\bar{2})]/8\sqrt{15}
\end{aligned}$$

TABLE 35--Continued

$$
\begin{aligned}
{}^{2}T^{C}_{1g}\text{-}1({}^{2}H) = {} & [-32(1\bar{0}-1)+16(\bar{1}0-1)-8\sqrt{6}(1\bar{1}-2)+8\sqrt{6}(2-1-\bar{1}) \\
& + 8(20-\bar{2})-16(2\bar{0}-2)+8(\bar{2}0-2)+16(10-\bar{1})+21\sqrt{6}(2\bar{2}\bar{1}) \\
& + 14(\bar{0}-\bar{1}-2)+14(0-\bar{1}-\bar{2})-28(\bar{0}-1-\bar{2})-7\sqrt{6}(\bar{1}-2-\bar{2})+8\sqrt{6}(1\bar{1}-\bar{1}) \\
& - 6\sqrt{6}(\bar{1}\bar{0}\bar{0})+12(\bar{2}\bar{0}-1)+6(2\bar{0}-\bar{1})-18(\bar{2}0-\bar{1})-4\sqrt{6}(\bar{2}1-\bar{2}) \\
& + \sqrt{6}(\bar{2}\bar{1}-2)+3\sqrt{6}(2\bar{1}-\bar{2})]/24\sqrt{14}
\end{aligned}
$$

$$
\begin{aligned}
{}^{2}T^{C}_{1g}\text{-}2({}^{2}H) = {} & [-24(2\bar{2}0)+8\sqrt{6}(21\bar{1})+24(0-2-\bar{2})-8\sqrt{6}(-1-\bar{1}-2) \\
& + 5\sqrt{6}(2\bar{2}\bar{1})-18(\bar{0}-\bar{1}-2)-18(0-\bar{1}-\bar{2})+36(\bar{0}-1-\bar{2})+9\sqrt{6}(\bar{1}-2-\bar{2}) \\
& + 8\sqrt{6}(1\bar{1}-\bar{1})-6\sqrt{6}(\bar{1}\bar{0}\bar{0})+12(\bar{2}\bar{0}-1)+6(2\bar{0}-\bar{1})-18(\bar{2}0-\bar{1}) \\
& - 4\sqrt{6}(\bar{2}1-\bar{2})+\sqrt{6}(\bar{2}\bar{1}-2)+3\sqrt{6}(2\bar{1}-\bar{2})]/24\sqrt{10}
\end{aligned}
$$

$$
\begin{aligned}
{}^{4}T^{C}_{1g}({}^{4}P) = {} & i[-4(10-\bar{1})-4(1\bar{0}-1)-4(\bar{1}0-1)+2(20-\bar{2}) \\
& + 2(2\bar{0}-2)+2(\bar{2}0-2)+2(2\bar{0}-\bar{1})+2(\bar{2}0-\bar{1})+2(\bar{2}\bar{0}-1) \\
& - \sqrt{6}(\bar{2}\bar{1}-2)-\sqrt{6}(\bar{2}1-\bar{2})-\sqrt{6}(2\bar{1}-\bar{2})+6(10-2)-3\sqrt{6}(2-1-2)]/6\sqrt{5}
\end{aligned}
$$

$$
\begin{aligned}
{}^{4}T^{C}_{1g}({}^{4}F) = {} & i[-4(10-\bar{1})-4(1\bar{0}-1)-4(\bar{1}0-1)-8(20-\bar{2})-8(2\bar{0}-2) \\
& - 8(\bar{2}0-2)-3(\bar{2}\bar{0}-1)-3(\bar{2}0-\bar{1})-3(2\bar{0}-\bar{1})-\sqrt{6}(\bar{2}\bar{1}-2) \\
& - \sqrt{6}(\bar{2}1-\bar{2})-\sqrt{6}(2\bar{1}-\bar{2})-5(\bar{0}-\bar{1}-2)-5(\bar{0}-1-\bar{2})-5(0-\bar{1}-\bar{2}) \\
& - 9(10-2)-3\sqrt{6}(2-1-2)-15(210)]/12\sqrt{5}
\end{aligned}
$$

$$
\begin{aligned}
{}^{4}T^{C}_{2g}({}^{4}F) = {} & [2\sqrt{6}(\bar{2}\bar{1}-\bar{1})+2\sqrt{6}(\bar{1}-\bar{1}-\bar{2})-3(10-2)-\sqrt{6}(2-1-2) \\
& + 3(210)+3(\bar{2}\bar{0}-1)+3(\bar{2}0-\bar{1})+3(2\bar{0}-\bar{1})+\sqrt{6}(\bar{2}\bar{1}-2) \\
& + \sqrt{6}(\bar{2}1-\bar{2})+\sqrt{6}(2\bar{1}-\bar{2})-3(\bar{0}-\bar{1}-2)-3(\bar{0}-1-\bar{2})-3(0-\bar{1}-\bar{2})]/12
\end{aligned}
$$

TABLE 35--Continued

Γ^{C}_{7a}

$$\begin{aligned}
{}^{2}A^{C}_{2g}({}^{2}F) = &-i[(\bar{2}\bar{1}-1)+2(2\bar{2}-\bar{2})-\sqrt{6}(1\bar{1}\bar{0})-(\bar{2}1-\bar{1})\\
&-\sqrt{6}(\bar{0}-1-\bar{1})-(1-\bar{1}-\bar{2})+2(\bar{2}-2-\bar{2})+(\bar{1}-1-\bar{2})]/2\sqrt{6}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}D\text{-}a) = &[(\bar{2}\bar{1}-1)+(\bar{2}0\bar{0})-(2\bar{2}-\bar{2})-(\bar{2}1-\bar{1})-(\bar{1}-1-\bar{2})\\
&-(0\bar{0}-\bar{2})+(\bar{2}-2-\bar{2})+(1-\bar{1}-\bar{2})+2(1\bar{1}-1)+2(10\bar{0})+2(\bar{2}1-2)\\
&-2(21-\bar{2})]/2\sqrt{6}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}D\text{-}b) = &[4(2\bar{1}-\bar{1})-5(2\bar{2}-\bar{2})-3(\bar{2}\bar{1}-1)-(\bar{2}1-\bar{1})\\
&-3(\bar{2}0\bar{0})-2\sqrt{6}(1\bar{1}\bar{0})-(\bar{1}-1-\bar{2})-3(1-\bar{1}-\bar{2})+5(\bar{2}-2-\bar{2})+3(0\bar{0}-\bar{2})\\
&+4(\bar{1}-\bar{1}-2)+2\sqrt{6}(\bar{0}-1-\bar{1})+6(21-\bar{2})+2(\bar{2}1-2)-8(2\bar{1}-2)\\
&-2(1\bar{1}-1)+6(10\bar{0})-4\sqrt{6}(\bar{2}0-1)+4\sqrt{6}(2\bar{0}-1)]/6\sqrt{14}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}F) = &\,i[2(\bar{2}\bar{1}-1)+4(2\bar{2}-\bar{2})-2\sqrt{6}(1\bar{1}\bar{0})-2(\bar{2}1-\bar{1})\\
&+2\sqrt{6}(\bar{0}-1-\bar{1})+2(1-\bar{1}-\bar{2})-4(\bar{2}-2-\bar{2})-2(\bar{1}-1-\bar{2})+4(1\bar{1}-1)\\
&-\sqrt{6}(2\bar{0}-1)-6(2\bar{1}-2)+4(\bar{2}1-2)-6(10\bar{0})+\sqrt{6}(20-\bar{1})\\
&+2(21-\bar{2})+2\sqrt{6}(0-1-\bar{2})-\sqrt{6}(0-\bar{1}-2)-6(1-2-\bar{2})-\sqrt{6}(\bar{0}-1-2)]/12\sqrt{2}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}G) = &[24(\bar{2}0\bar{0})+24(2\bar{1}-\bar{1})+2\sqrt{6}(1\bar{1}\bar{0})-18(\bar{2}\bar{1}-1)\\
&-6(\bar{2}1-\bar{1})+12(2\bar{2}-\bar{2})-2\sqrt{6}(\bar{0}-1-\bar{1})-6(\bar{1}-1-\bar{2})-18(1-\bar{1}-\bar{2})\\
&-12(\bar{2}-2-\bar{2})-24(0\bar{0}-\bar{2})+24(\bar{1}-\bar{1}-2)-6(10\bar{0})+3\sqrt{6}(2\bar{0}-1)\\
&-7\sqrt{6}(20-\bar{1})-6(21-\bar{2})-12(1\bar{1}-1)+4\sqrt{6}(\bar{2}0-1)+12(\bar{2}1-2)\\
&-6(2\bar{1}-2)+7\sqrt{6}(0-\bar{1}-2)+14\sqrt{6}(0-1-\bar{2})+42(1-2-\bar{2})\\
&-21\sqrt{6}(\bar{0}-1-2)]/4\sqrt{630}
\end{aligned}$$

TABLE 35--Continued

$$\begin{aligned}
{}^2T^C_{2g}({}^2H) &= i[2\sqrt{6}(1\bar{1}\bar{0})-6(\bar{2}0\bar{0})-6(\bar{2}1-\bar{1})+2(\bar{2}\bar{1}-1)\\
&+ 4(2\bar{1}-\bar{1})+2(2\bar{2}-\bar{2})-2\sqrt{6}(\bar{0}-1-\bar{1})+6(0\bar{0}-\bar{2})-6(\bar{1}-1-\bar{2})\\
&+ 4(\bar{1}-\bar{1}-2)+2(1-\bar{1}-\bar{2})-2(\bar{2}-2-\bar{2})-15(2\bar{2}1)+2\sqrt{6}(0-\bar{1}-2)\\
&- \sqrt{6}(0-1-\bar{2})-\sqrt{6}(\bar{0}-1-2)-3(1-2-\bar{2})+8(1\bar{1}-1)-6(10\bar{0})\\
&+ 3\sqrt{6}(2\bar{0}-1)-2\sqrt{6}(20-\bar{1})-(21-\bar{2})+4(2\bar{1}-2)-\sqrt{6}(\bar{2}0-1)\\
&- 3(\bar{2}1-2)]/12\sqrt{5}
\end{aligned}$$

$$\begin{aligned}
{}^4T^C_{1g}({}^4P) &= i[4(10-1)-2(20-2)-2(\bar{1}\bar{0}-\bar{2})+\sqrt{6}(\bar{2}-\bar{1}-\bar{2})\\
&+ 2(20-\bar{1})+2(2\bar{0}-1)+2(\bar{2}0-1)-\sqrt{6}(21-\bar{2})-\sqrt{6}(2\bar{1}-2)\\
&- \sqrt{6}(\bar{2}1-2)]/\sqrt{60}
\end{aligned}$$

$$\begin{aligned}
{}^4T^C_{1g}({}^4F) &= i[4(10-1)+8(20-2)+3(\bar{1}\bar{0}-\bar{2})+\sqrt{6}(\bar{2}-\bar{1}-\bar{2})\\
&+ 5(\bar{2}\bar{1}\bar{0})-3(20-\bar{1})-3(2\bar{0}-1)-3(\bar{2}0-1)-\sqrt{6}(\bar{2}1-2)\\
&- \sqrt{6}(2\bar{1}-2)-\sqrt{6}(21-\bar{2})-5(\bar{0}-1-2)-5(0-\bar{1}-2)\\
&- 5(0-1-\bar{2})]/4\sqrt{15}
\end{aligned}$$

$$\begin{aligned}
{}^4T^C_{2g}({}^4F) &= [-4(\bar{2}\bar{1}-1)-4(\bar{2}1-\bar{1})-4(2\bar{1}-\bar{1})-4(\bar{1}-\bar{1}-2)\\
&- 4(\bar{1}-1-\bar{2})-4(1-\bar{1}-\bar{2})+\sqrt{6}(\bar{2}0-1)+\sqrt{6}(2\bar{0}-1)+\sqrt{6}(20-\bar{1})\\
&+ 2(\bar{2}1-2)+2(2\bar{1}-2)+2(21-\bar{2})-\sqrt{6}(\bar{0}-1-2)-\sqrt{6}(0-\bar{1}-2)\\
&- \sqrt{6}(0-1-\bar{2})+3\sqrt{6}(\bar{1}\bar{0}-\bar{2})+6(\bar{2}-\bar{1}-\bar{2})-3\sqrt{6}(\bar{2}\bar{1}\bar{0})]/12\sqrt{2}
\end{aligned}$$

TABLE 35--Continued

Γ^{C}_{8a}

$^{2}E^{C}_{g}(^{2}D\text{-}a) = [-(10-\bar{1})-(\bar{2}0-2)+(\bar{1}0-1)+(20-\bar{2})]/2$

$^{2}E^{C}_{g}(^{2}D\text{-}b) = [-3(20-\bar{2})+2\sqrt{6}(1\bar{1}-2)+3(\bar{2}0-2)+3(\bar{1}0-1)$
$- 3(10-\bar{1})+2\sqrt{6}(2-1-\bar{1})]/\sqrt{84}$

$^{2}E^{C}_{g}(^{2}G) = [-10(10-\bar{1})-5\sqrt{6}(2-1-\bar{1})-10(20-\bar{2})+10(\bar{1}0-1)$
$- 5\sqrt{6}(1\bar{1}-2)+10(\bar{2}0-2)+14(2\overline{20})+7\sqrt{6}(21\bar{1})+7\sqrt{6}(-1-\bar{1}-2)$
$+ 14(0-2-\bar{2})]/4\sqrt{105}$

$^{2}E^{C}_{g}(^{2}H) = i[3(2\overline{20})-\sqrt{6}(21\bar{1})+3(0-2-\bar{2})-\sqrt{6}(-1-\bar{1}-2)]/\sqrt{30}$

$^{2}T^{C}_{1g}(^{2}P) = [8(20-\bar{2})+6\sqrt{6}(1\bar{1}-2)-16(2\bar{0}-2)+8(\bar{2}0-2)$
$+ 2(10-\bar{1})-6\sqrt{6}(2-1-\bar{1})-4(1\bar{0}-1)+2(\bar{1}0-1)+2\sqrt{6}(\bar{2}1-\bar{2})$
$+ 2\sqrt{6}(2\bar{1}-\bar{2})-4\sqrt{6}(\overline{21}-2)-10(2\bar{0}-\bar{1})+8(\overline{20}-1)+2(\bar{2}0-\bar{1})$
$+ 3\sqrt{6}(1\bar{1}-\bar{1})+3\sqrt{6}(\overline{100})]/6\sqrt{35}$

$^{2}T^{C}_{1g}(^{2}F) = [-8(\bar{1}0-1)+16(1\bar{0}-1)-4\sqrt{6}(1\bar{1}-2)+4\sqrt{6}(2-1-\bar{1})$
$- 16(2\bar{0}-2)+8(\bar{2}0-2)-8(10-\bar{1})+8(20-\bar{2})-2\sqrt{6}(1\bar{1}-\bar{1})+3(\overline{20}-1)$
$+ \sqrt{6}(\overline{21}-2)+2\sqrt{6}(2\bar{1}-\bar{2})-3\sqrt{6}(\bar{2}1-\bar{2})+3\sqrt{6}(\overline{100})-3(\bar{2}0-\bar{1})$
$+ 5(\bar{0}-1-\bar{2})+5(0-\bar{1}-\bar{2})-10(\bar{0}-\bar{1}-2)-5\sqrt{6}(\bar{1}-2-\bar{2})]/12\sqrt{10}$

TABLE 35--Continued

$$\begin{aligned}
{}^{2}T^{C}_{1g}({}^{2}G) &= i[-4\sqrt{6}(-1-\bar{1}-2)-8(0-2-\bar{2})+8(2\bar{2}0)+4\sqrt{6}(21\bar{1})\\
&- \sqrt{6}(\bar{1}\bar{0}\bar{0})+7(\bar{2}\bar{0}-1)-3(\bar{2}0-\bar{1})-4(2\bar{0}-\bar{1})-2\sqrt{6}(2\bar{1}-\bar{2})\\
&- 2\sqrt{6}(1\bar{1}-\bar{1})+\sqrt{6}(\bar{2}\bar{1}-2)+\sqrt{6}(\bar{2}1-\bar{2})-3(0-\bar{1}-\bar{2})-\sqrt{6}(\bar{1}-2-\bar{2})\\
&+ 2(\bar{0}-\bar{1}-2)+(\bar{0}-1-\bar{2})]/4\sqrt{30}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{1g}\text{-}1({}^{2}H) &= [-64(1\bar{0}-1)+32(\bar{1}0-1)-16\sqrt{6}(1\bar{1}-2)+16\sqrt{6}(2-1-\bar{1})\\
&+ 16(20-\bar{2})-32(2\bar{0}-2)+16(\bar{2}0-2)+32(10-\bar{1})-21\sqrt{6}(2\bar{2}\bar{1})\\
&- 14(\bar{0}-\bar{1}-2)-14(0-\bar{1}-\bar{2})+28(\bar{0}-1-\bar{2})+7\sqrt{6}(\bar{1}-2-\bar{2})-8\sqrt{6}(1\bar{1}-\bar{1})\\
&+ 6\sqrt{6}(\bar{1}\bar{0}\bar{0})-12(\bar{2}\bar{0}-1)-6(2\bar{0}-\bar{1})+18(\bar{2}0-\bar{1})+4\cdot\sqrt{6}(\bar{2}1-\bar{2})\\
&- \sqrt{6}(\bar{2}\bar{1}-2)-3\sqrt{6}(2\bar{1}-\bar{2})]/48\sqrt{7}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{1g}\text{-}2({}^{2}H) &= [-48(2\bar{2}0)+16\sqrt{6}(21\bar{1})+48(0-2-\bar{2})\\
&- 16\sqrt{6}(-1-\bar{1}-2)-5\sqrt{6}(2\bar{2}\bar{1})+18(\bar{0}-\bar{1}-2)+18(0-\bar{1}-\bar{2})\\
&- 36(\bar{0}-1-\bar{2})-9\sqrt{6}(\bar{1}-2-\bar{2})-8\sqrt{6}(1\bar{1}-\bar{1})+6\sqrt{6}(\bar{1}\bar{0}\bar{0})\\
&- 12(\bar{2}\bar{0}-1)-6(2\bar{0}-\bar{1})+18(\bar{2}0-\bar{1})+4\sqrt{6}(\bar{2}1-\bar{2})-\sqrt{6}(\bar{2}\bar{1}-2)\\
&- 3\sqrt{6}(2\bar{1}-\bar{2})]/48\sqrt{5}
\end{aligned}$$

$$ {}^{2}T^{C}_{2g}({}^{2}D\text{-}a) = [(1\bar{1}-\bar{1})+(\bar{1}\bar{0}\bar{0})+(\bar{2}\bar{1}-2)-(2\bar{1}-\bar{2})]/2 $$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}D\text{-}b) &= [4(\bar{2}1-\bar{2})-3(\bar{2}\bar{1}-2)-(2\bar{1}-\bar{2})-(1\bar{1}-\bar{1})+3(\bar{1}\bar{0}\bar{0})\\
&- 2\sqrt{6}(\bar{2}0-\bar{1})+2\sqrt{6}(2\bar{0}-\bar{1})]/\sqrt{84}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}F) &= i[4(1\bar{1}-\bar{1})-\sqrt{6}(\bar{2}\bar{0}-1)-2(\bar{2}\bar{1}-2)-4(2\bar{1}-\bar{2})\\
&+ 6(\bar{2}1-\bar{2})-6(\bar{1}\bar{0}\bar{0})+\sqrt{6}(\bar{2}0-\bar{1})+\sqrt{6}(\bar{0}-1-\bar{2})+\sqrt{6}(0-\bar{1}-\bar{2})\\
&- 2\sqrt{6}(\bar{0}-\bar{1}-2)-6(\bar{1}-2-\bar{2})]/8\sqrt{3}
\end{aligned}$$

TABLE 35--Continued

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}G) &= [-\sqrt{6}(\bar{1}0\bar{0})+7(\bar{2}\bar{0}-1)-3(\bar{2}0-\bar{1})-4(2\bar{0}-\bar{1}) \\
&- 2\sqrt{6}(2\bar{1}-\bar{2})-2\sqrt{6}(1\bar{1}-\bar{1})+\sqrt{6}(\bar{2}\bar{1}-2)+\sqrt{6}(\bar{2}1-\bar{2})+21(0-\bar{1}-\bar{2}) \\
&+ 7\sqrt{6}(\bar{1}-2-\bar{2})-14(\bar{0}-\bar{1}-2)-7(\bar{0}-1-\bar{2})]/4\sqrt{70}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}H) &= i[-30(2\bar{2}\bar{1})+2\sqrt{6}(\bar{0}-\bar{1}-2)+2\sqrt{6}(0-\bar{1}-\bar{2})-4\sqrt{6}(\bar{0}-1-\bar{2}) \\
&- 6(\bar{1}-2-\bar{2})+16(1\bar{1}-\bar{1})-12(\bar{1}0\bar{0})+4\sqrt{6}(\bar{2}\bar{0}-1)+2\sqrt{6}(2\bar{0}-\bar{1}) \\
&- 6\sqrt{6}(\bar{2}0-\bar{1})-8(\bar{2}1-\bar{2})+2(\bar{2}\bar{1}-2)+6(2\bar{1}-\bar{2})]/8\sqrt{30}
\end{aligned}$$

$$\begin{aligned}
{}^{4}A^{C}_{2g}({}^{4}F) &= i[(\bar{1}-\bar{1}-\bar{2})-(\bar{2}\bar{1}-\bar{1})/\sqrt{2}
\end{aligned}$$

$$\begin{aligned}
(1)\,{}^{4}T^{C}_{1g}({}^{4}P) &= i[4(\bar{1}0-1)+4(1\bar{0}-1)+4(10-\bar{1})-2(\bar{2}0-2) \\
&- 2(2\bar{0}-2)-2(20-\bar{2})+4(\bar{2}\bar{0}-1)+4(\bar{2}0-\bar{1})+4(2\bar{0}-\bar{1}) \\
&- 2\sqrt{6}(\bar{2}\bar{1}-2)-2\sqrt{6}(\bar{2}1-\bar{2})-2\sqrt{6}(2\bar{1}-\bar{2})]/6\sqrt{5}
\end{aligned}$$

$$\begin{aligned}
(2)\,{}^{4}T^{C}_{1g}({}^{4}P) &= i[4(\bar{1}0-1)+4(1\bar{0}-1)+4(10-\bar{1})-2(\bar{2}0-2) \\
&- 2(2\bar{0}-2)-2(20-\bar{2})-2(\bar{2}\bar{0}-1)-2(\bar{2}0-\bar{1})-2(2\bar{0}-\bar{1}) \\
&+ \sqrt{6}(\bar{2}\bar{1}-2)+\sqrt{6}(\bar{2}1-\bar{2})+\sqrt{6}(2\bar{1}-\bar{2})+6(10-2) \\
&- 3\sqrt{6}(2-1-2)]/6\sqrt{5}
\end{aligned}$$

$$\begin{aligned}
(1)\,{}^{4}T^{C}_{1g}({}^{4}F) &= i[2(\bar{1}0-1)+2(1\bar{0}-1)+2(10-\bar{1})+4(\bar{2}0-2) \\
&+ 4(2\bar{0}-2)+4(20-\bar{2})-3(\bar{2}\bar{0}-1)-3(\bar{2}0-\bar{1})-3(2\bar{0}-\bar{1}) \\
&- \sqrt{6}(\bar{2}\bar{1}-2)-\sqrt{6}(\bar{2}1-\bar{2})-\sqrt{6}(2\bar{1}-\bar{2})-5(\bar{0}-\bar{1}-2)-5(\bar{0}-1-\bar{2}) \\
&- 5(0-\bar{1}-\bar{2})]/6\sqrt{5}
\end{aligned}$$

TABLE 35--Continued

$$\begin{aligned}(2)\,{}^4T^C_{1g}({}^4F) = {} & i[4(\bar{1}0-1)+4(1\bar{0}-1)+4(10-\bar{1})+8(\bar{2}0-2) \\ & + 8(2\bar{0}-2)+8(20-\bar{2})+3(\bar{2}\bar{0}-1)+3(\bar{2}0-\bar{1})+3(2\bar{0}-\bar{1}) \\ & + \sqrt{6}(\bar{2}\bar{1}-2)+\sqrt{6}(\bar{2}1-\bar{2})+\sqrt{6}(2\bar{1}-\bar{2})+5(\bar{0}-\bar{1}-2)+5(\bar{0}-1-\bar{2}) \\ & + 5(0-\bar{1}-\bar{2})-9(10-2)-3\sqrt{6}(2-1-2)-15(210)]/12\sqrt{5}\end{aligned}$$

$$\begin{aligned}(1)\,{}^4T^C_{2g}({}^4F) = {} & [-2(\bar{2}\bar{1}-\bar{1})-2(\bar{1}-\bar{1}-\bar{2})-\sqrt{6}(10-2)-2(2-1-2) \\ & + \sqrt{6}(210)]/2\sqrt{6}\end{aligned}$$

$$\begin{aligned}(2)\,{}^4T^C_{2g}({}^4F) = {} & [2\sqrt{6}(\bar{2}\bar{1}-\bar{1})+2\sqrt{6}(\bar{1}-\bar{1}-\bar{2})-3(10-2)-\sqrt{6}(2-1-2) \\ & + 3(210)-3(\bar{2}\bar{0}-1)-3(\bar{2}0-\bar{1})-3(2\bar{0}-\bar{1})-\sqrt{6}(\bar{2}\bar{1}-2) \\ & - \sqrt{6}(\bar{2}1-\bar{2})-\sqrt{6}(2\bar{1}-\bar{2})+3(\bar{0}-\bar{1}-2)+3(\bar{0}-1-\bar{2})+3(0-\bar{1}-\bar{2})]/12\end{aligned}$$

Γ^C_{8c}

$$\begin{aligned}{}^2E^C_g({}^2D\text{-}a) = {} & [(\bar{2}\bar{1}-1)+(\bar{2}0\bar{0})-(2\bar{2}-\bar{2})-(\bar{2}1-\bar{1})+(\bar{1}-1-\bar{2}) \\ & + (0\bar{0}-\bar{2})-(\bar{2}-2-\bar{2})-(1-\bar{1}-\bar{2})]/\sqrt{8}\end{aligned}$$

$$\begin{aligned}{}^2E^C_g({}^2D\text{-}b) = {} & [4(2\bar{1}-\bar{1})-5(2\bar{2}-\bar{2})-3(\bar{2}\bar{1}-1)-(\bar{2}1-\bar{1}) \\ & - 3(\bar{2}0\bar{0})-2\sqrt{6}(1\bar{1}\bar{0})+(\bar{1}-1-\bar{2})+3(1-\bar{1}-\bar{2})-5(\bar{2}-2-\bar{2}) \\ & - 3(0\bar{0}-\bar{2})-4(\bar{1}-\bar{1}-2)-2\sqrt{6}(\bar{0}-1-\bar{1})]/2\sqrt{42}\end{aligned}$$

$$\begin{aligned}{}^2E^C_g({}^2G) = {} & [-12(\bar{2}0\bar{0})-12(2\bar{1}-\bar{1})-\sqrt{16}(1\bar{1}\bar{0})+9(\bar{2}\bar{1}-1) \\ & + 3(\bar{2}1-\bar{1})-6(2\bar{2}-\bar{2})-\sqrt{6}(\bar{0}-1-\bar{1})-3(\bar{1}-1-\bar{2})-9(1-\bar{1}-\bar{2}) \\ & - 6(\bar{2}-2-\bar{2})-12(0\bar{0}-\bar{2})+12(\bar{1}-\bar{1}-2)]/\sqrt{840}\end{aligned}$$

TABLE 35--Continued

$$\begin{aligned}
{}^2E_g^C({}^2H) &= -i[-\sqrt{6}(1\bar{1}\bar{0})+3(\bar{2}0\bar{0})+3(\bar{2}1\text{-}\bar{1})-(\bar{2}\bar{1}\text{-}1) \\
&- 2(2\bar{1}\text{-}\bar{1})-(2\bar{2}\text{-}\bar{2})-\sqrt{6}(\bar{0}\text{-}1\text{-}\bar{1})+3(0\bar{0}\text{-}\bar{2})-3(\bar{1}\text{-}1\text{-}\bar{2}) \\
&+ 2(\bar{1}\text{-}\bar{1}\text{-}2)+(1\text{-}\bar{1}\text{-}\bar{2})-(\bar{2}\text{-}2\text{-}\bar{2})]/\sqrt{60}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1g}^C({}^2P) &= [12(21\text{-}\bar{2})-6(2\bar{1}\text{-}2)-6(\bar{2}1\text{-}2)-4\sqrt{6}(20\text{-}\bar{1}) \\
&- \sqrt{6}(2\bar{0}\text{-}1)+5\sqrt{6}(\bar{2}0\text{-}1)+9(1\bar{1}\text{-}1)+9(10\bar{0})]/\sqrt{630}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1g}^C({}^2F) &= [-2\sqrt{6}(1\bar{1}\text{-}1)+3(2\bar{0}\text{-}1)+3\sqrt{6}(2\bar{1}\text{-}2)-2\sqrt{6}(\bar{2}1\text{-}2) \\
&+ 3\sqrt{6}(10\bar{0})-3(20\text{-}\bar{1})-\sqrt{6}(21\text{-}\bar{2})+10(0\text{-}1\text{-}\bar{2})-5(0\text{-}\bar{1}\text{-}2) \\
&- 5\sqrt{6}(1\text{-}2\text{-}\bar{2})-5(\bar{0}\text{-}1\text{-}2)/4\sqrt{30}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1g}^C({}^2G) &= -i[\sqrt{6}(10\bar{0})-3(2\bar{0}\text{-}1)+7(20\text{-}\bar{1})+\sqrt{6}(21\text{-}\bar{2}) \\
&+ 2\sqrt{6}(1\bar{1}\text{-}1)-4(\bar{2}0\text{-}1)-2\sqrt{6}(\bar{2}1\text{-}2)+\sqrt{6}(2\bar{1}\text{-}2)+(0\text{-}\bar{1}\text{-}2) \\
&+ 2(0\text{-}1\text{-}\bar{2})+\sqrt{6}(1\text{-}2\text{-}\bar{2})-3(\bar{0}\text{-}1\text{-}2)]/4\sqrt{10}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1g}^C\text{-}1({}^2H) &= [-21\sqrt{6}(2\bar{2}\bar{1})-28(0\text{-}\bar{1}\text{-}2)+14(0\text{-}1\text{-}\bar{2}) \\
&+ 14(\bar{0}\text{-}1\text{-}2)+7\sqrt{6}(1\text{-}2\text{-}\bar{2})-8\sqrt{6}(1\bar{1}\text{-}1)+6\sqrt{6}(10\bar{0})-18(2\bar{0}\text{-}1) \\
&+ 12(20\text{-}\bar{1})+\sqrt{6}(21\text{-}\bar{2})-4\sqrt{6}(2\bar{1}\text{-}2)+6(\bar{2}0\text{-}1) \\
&+ 3\sqrt{6}(\bar{2}1\text{-}2)]/8\sqrt{84}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1g}^C\text{-}2({}^2H) &= [-15(2\bar{2}\bar{1})+18\sqrt{6}(0\text{-}\bar{1}\text{-}2)-9\sqrt{6}(0\text{-}1\text{-}\bar{2}) \\
&- 9\sqrt{6}(\bar{0}\text{-}1\text{-}2)-27(1\text{-}2\text{-}\bar{2})-24(1\bar{1}\text{-}1)+18(10\bar{0})-9\sqrt{6}(2\bar{0}\text{-}1) \\
&+ 6\sqrt{6}(20\text{-}\bar{1})+3(21\text{-}\bar{2})-12(2\bar{1}\text{-}2)+3\sqrt{6}(\bar{2}0\text{-}1) \\
&+ 9(\bar{2}1\text{-}2)]/8\sqrt{90}
\end{aligned}$$

TABLE 35--Continued

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}D\text{-}a) = {} & [-(\overline{1}-1-\overline{2})-(0\overline{0}-\overline{2})+(\overline{2}-2-\overline{2})+(1-\overline{1}-\overline{2}) \\
& + (\overline{2}\overline{1}-1)+(\overline{2}0\overline{0})-(2\overline{2}-\overline{2})-(\overline{2}1-\overline{1})-(1\overline{1}-1)-(10\overline{0}) \\
& - (\overline{2}1-2)+(21-\overline{2})]/2\sqrt{3}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}D\text{-}b) = {} & [-(\overline{1}-1-\overline{2})-3(1-\overline{1}-\overline{2})+5(\overline{2}-2-\overline{2})+3(0\overline{0}-\overline{2}) \\
& + 4(\overline{1}-\overline{1}-2)+2\sqrt{6}(\overline{0}-1-\overline{1})+4(2\overline{1}-\overline{1})-5(2\overline{2}-\overline{2}))-3(\overline{2}\overline{1}-1) \\
& - (\overline{2}1-\overline{1})-3(\overline{2}0\overline{0})-2\sqrt{6}(1\overline{1}\overline{0})-3(21-\overline{2})-(\overline{2}1-2) \\
& + 4(2\overline{1}-2)+(1\overline{1}-1)-3(10\overline{0})+2\sqrt{6}(\overline{2}0-1)-2\sqrt{6}(2\overline{0}-1)]/6\sqrt{7}
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}F) = {} & i[4(\overline{2}\overline{1}-1)+8(2\overline{2}-\overline{2})-4\sqrt{6}(1\overline{1}\overline{0})-4(\overline{2}1-\overline{1}) \\
& + 4(1-\overline{1}-\overline{2})+4\sqrt{6}(\overline{0}-1-\overline{1})-8(\overline{2}-2-\overline{2})-4(\overline{1}-1-\overline{2})-4(1\overline{1}-1) \\
& + \sqrt{6}(2\overline{0}-1)+6(2\overline{1}-2)-4(\overline{2}1-2)+6(10\overline{0})-\sqrt{6}(20-\overline{1}) \\
& - 2(21-\overline{2})-2\sqrt{6}(0-1-\overline{2})+\sqrt{6}(0-\overline{1}-2)+6(1-2-\overline{2}) \\
& + \sqrt{6}(\overline{0}-1-2)]/24
\end{aligned}$$

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}G) = {} & [-4(\overline{0}-1-\overline{1})-2\sqrt{6}(\overline{1}-1-\overline{2})-6\sqrt{6}(1-\overline{1}-\overline{2})-4\sqrt{6}(\overline{2}-2-\overline{2}) \\
& - 8\sqrt{6}(0\overline{0}-\overline{2})+8\sqrt{6}(\overline{1}-\overline{1}-2)+8\sqrt{6}(\overline{2}0\overline{0})+8\sqrt{6}(2\overline{1}-\overline{1}) \\
& + 4(1\overline{1}\overline{0})-6\sqrt{6}(\overline{2}\overline{1}-1)-2\sqrt{6}(\overline{2}1-\overline{1})+4\sqrt{6}(2\overline{2}-\overline{2})+\sqrt{6}(10\overline{0}) \\
& - 3(2\overline{0}-1)+7(20-\overline{1})+\sqrt{6}(21-\overline{2})+2\sqrt{6}(1\overline{1}-1)-4(\overline{2}0-1) \\
& - 2\sqrt{6}(\overline{2}1-2)+\sqrt{6}(2\overline{1}-2)-7(0-\overline{1}-2)-14(0-1-\overline{2}) \\
& - 7\sqrt{6}(1-2-\overline{2})+21(\overline{0}-1-2)]/4\sqrt{210}
\end{aligned}$$

TABLE 35--Continued

$$\begin{aligned}
{}^{2}T^{C}_{2g}({}^{2}H) &= i[4\sqrt{6}(1\bar{1}\bar{0})-12(\bar{2}\bar{0}\bar{0})-12(\bar{2}1-\bar{1})+4(\bar{2}\bar{1}-1)\\
&+ 8(2\bar{1}-\bar{1})+4(2\bar{2}-\bar{2})-4\sqrt{6}(\bar{0}-1-\bar{1})+12(0\bar{0}-\bar{2})-12(\bar{1}-1-\bar{2})\\
&+ 8(\bar{1}-\bar{1}-2)+4(1-\bar{1}-\bar{2})-4(\bar{2}-2-\bar{2})+15(2\bar{2}1)-2\sqrt{6}(0-\bar{1}-2)\\
&+ \sqrt{6}(0-1-\bar{2})+\sqrt{6}(\bar{0}-1-2)+3(1-2-\bar{2})-8(1\bar{1}-1)+6(1\bar{0}\bar{0})\\
&- 3\sqrt{6}(2\bar{0}-1)+2\sqrt{6}(20-\bar{1})+(21-\bar{2})-4(2\bar{1}-2)\\
&+ \sqrt{6}(\bar{2}0-1)+3(\bar{2}1-2)]/12\sqrt{10}
\end{aligned}$$

$$\begin{aligned}
{}^{4}A^{C}_{2g}({}^{4}F) &= i[(\bar{2}\bar{1}-1)+(\bar{2}1-\bar{1})+(2\bar{1}-\bar{1})-(\bar{1}-\bar{1}-2)\\
&- (\bar{1}-1-\bar{2})-(1-\bar{1}-\bar{2})]/\sqrt{6}
\end{aligned}$$

$$(1)\,{}^{4}T^{C}_{1g}({}^{4}P) = i[-2(10-1)+(20-2)-2(\bar{1}\bar{0}-\bar{2})+\sqrt{6}(\bar{2}-\bar{1}-\bar{2})]/\sqrt{15}$$

$$\begin{aligned}
(2)\,{}^{4}T^{C}_{1g}({}^{4}P) &= i[4(10-1)-2(20-2)-2(\bar{1}\bar{0}-\bar{2})+\sqrt{6}(\bar{2}-\bar{1}-\bar{2})-2(\bar{2}0-1)\\
&- 2(2\bar{0}-1)-2(20-\bar{1})+\sqrt{6}(\bar{2}1-2)+\sqrt{6}(2\bar{1}-2)+\sqrt{6}(21-\bar{2})]/\sqrt{60}
\end{aligned}$$

$$\begin{aligned}
(1)\,{}^{4}T^{C}_{1g}({}^{4}F) &= i[-2(10-1)-4(20-2)+3(\bar{1}\bar{0}-\bar{2})+\sqrt{6}(\bar{2}-\bar{1}-\bar{2})\\
&+ 5(\bar{2}\bar{1}\bar{0})]/\sqrt{60}
\end{aligned}$$

$$\begin{aligned}
(2)\,{}^{4}T^{C}_{1g}({}^{4}F) &= i[4(10-1)+8(20-2)+3(\bar{1}\bar{0}-\bar{2})+\sqrt{6}(\bar{2}-\bar{1}-\bar{2})\\
&+ 5(\bar{2}\bar{1}\bar{0})+3(\bar{2}0-1)+3(2\bar{0}-1)+3(20-\bar{1})+\sqrt{6}(\bar{2}1-2)\\
&+ \sqrt{6}(2\bar{1}-2)+\sqrt{6}(21-\bar{2})+5(\bar{0}-1-2)+5(0-\bar{1}-2)+5(0-1-\bar{2})]/4\sqrt{15}
\end{aligned}$$

$$\begin{aligned}
(1)\,{}^{4}T^{C}_{2g}({}^{4}F) &= [-2(\bar{2}\bar{1}-1)-2(\bar{2}1-\bar{1})-2(2\bar{1}-\bar{1})-2(\bar{1}-\bar{1}-2)\\
&- 2(\bar{1}-1-\bar{2})-2(1-\bar{1}-\bar{2})+\sqrt{6}(\bar{0}-1-2)+\sqrt{6}(0-\bar{1}-2)+\sqrt{6}(0-1-\bar{2})\\
&- \sqrt{6}(\bar{2}0-1)-\sqrt{6}(2\bar{0}-1)-\sqrt{6}(20-\bar{1})-2(\bar{2}1-2)-2(2\bar{1}-2)\\
&- 2(21-\bar{2})]/6\sqrt{2}
\end{aligned}$$

TABLE 35--Continued

$$
\begin{aligned}
(2)\,{}^{4}T^{C}_{2g}({}^{4}F) = {} & [-12(\overline{21}-1)-12(\overline{2}1-\overline{1})-12(2\overline{1}-\overline{1})-12(\overline{1}-\overline{1}-2) \\
& - 12(\overline{1}-1-\overline{2})-12(1-\overline{1}-\overline{2})+3\sqrt{6}(\overline{2}0-1)+3\sqrt{6}(2\overline{0}-1) \\
& + 3\sqrt{6}(20-\overline{1})+6(\overline{2}1-2)+6(2\overline{1}-2)+6(21-\overline{2})-3\sqrt{6}(\overline{0}-1-2) \\
& - 3\sqrt{6}(0-\overline{1}-2)-3\sqrt{6}(0-1-\overline{2})-9\sqrt{6}(\overline{10}-\overline{2})-18(\overline{2}-\overline{1}-\overline{2}) \\
& + 9\sqrt{6}(\overline{210})]/36\sqrt{2}
\end{aligned}
$$

TABLE 36

a) Numbering of the Eigenvectors of the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme for the Spin-Orbit Perturbation

---

Γ_6^C

---

(1) = $^2A^C_{1g}(^2G)$

(2) = $^2T^C_{1g}(^2P)$

(3) = $^2T^C_{1g}(^2F)$

(4) = $^2T^C_{1g}(^2G)$

(5) = $^2T^C_{1g}\text{-}1(^2H)$

(6) = $^2T^C_{1g}\text{-}2(^2H)$

(7) = $^4T^C_{1g}(^4P)$

(8) = $^4T^C_{1g}(^4F)$

(9) = $^4T^C_{2g}(^4F)$

Γ_7^C

---

(1) = $^2A^C_{2g}(^2F)$

(2) = $^2T^C_{2g}(^2D\text{-}a)$

(3) = $^2T^C_{2g}(^2D\text{-}b)$

(4) = $^2T^C_{2g}(^2F)$

(5) = $^2T^C_{2g}(^2G)$

(6) = $^2T^C_{2g}(^2H)$

(7) = $^4T^C_{1g}(^4P)$

(8) = $^4T^C_{1g}(^4F)$

(9) = $^4T^C_{2g}(^4F)$

TABLE 36--Continued

Γ_8^C

(1) = ${}^2E_g^C({}^2D\text{-a})$

(2) = ${}^2E_g^C({}^2D\text{-b})$

(3) = ${}^2E_g^C({}^2G)$

(4) = ${}^2E_g^C({}^2H)$

(5) = ${}^2T_{1g}^C({}^2P)$

(6) = ${}^2T_{1g}^C({}^2F)$

(7) = ${}^2T_{1g}^C({}^2G)$

(8) = ${}^2T_{1g}^C\text{-}1({}^2H)$

(9) = ${}^2T_{1g}^C\text{-}2({}^2H)$

(10) = ${}^2T_{2g}^C({}^2D\text{-a})$

(11) = ${}^2T_{2g}^C({}^2D\text{-b})$

(12) = ${}^2T_{2g}^C({}^2F)$

(13) = ${}^2T_{2g}^C({}^2G)$

(14) = ${}^2T_{2g}^C({}^2H)$

(15) = ${}^4A_{2g}^C({}^4F)$

(16) = $(1){}^4T_{1g}^C({}^4P)$

(17) = $(2){}^4T_{1g}^C({}^4P)$

(18) = $(1){}^4T_{1g}^C({}^4F)$

(19) = $(2){}^4T_{1g}^C({}^4F)$

(20) = $(1){}^4T_{2g}^C({}^4F)$

(21) = $(2){}^4T_{2g}^C({}^4F)$

TABLE 36--Continued

b) The Non-Zero Matrix Elements (H'_{jk}'s) for
the Spin-Orbit Perturbation of the
$\{L, S, \chi^C, \chi^Q, \Gamma^Q\}$ Coupling Scheme

Γ_6^C

j	k	ζ	j	k	ζ
1	3	$\sqrt{15}/6$	6	6	$11/40$
1	4	$3i/2\sqrt{5}$	7	7	$-5/6$
1	5	$7/\sqrt{42}$	8	8	$5/4$
1	6	$3/\sqrt{30}$	8	9	$i\sqrt{5}/4$
1	8	$-i\sqrt{15}/3$	9	9	$1/4$
2	2	$-2/3$			
2	7	$i\sqrt{14}/3$			
3	3	$-1/4$			
3	4	$-5i/4\sqrt{3}$			
3	8	$i/4$			
3	9	$\sqrt{5}/4$			
4	4	$-3/20$			
4	5	$-14i\sqrt{210}$			
4	6	$-i\sqrt{6}/5$			
4	8	$-5/4\sqrt{3}$			
4	9	$-i\sqrt{15}/4$			
5	5	$-3/8$			
5	6	$-21/8\sqrt{35}$			

TABLE 36--Continued

Γ_7^C

j	k	ζ
1	2	-i
1	3	-i/√21
1	4	-1/2√3
1	5	i√105/14
1	9	i/√3
2	2	1/2
2	3	-√21/6
2	4	-2i/√3
2	7	6i/√15
2	8	3i/√15
2	9	-1/√3
3	3	-1/6
3	4	-2i/3√7
3	8	-5i/√35
3	9	5/3√7
4	4	1/12
4	5	15i/4√35
4	8	-√5/4
4	9	i/12
5	5	-3/4
5	8	-5i/4√7
5	9	-15/4√35
6	6	1/2
7	7	1/2
8	8	-3/4
8	9	-i√5/4
9	9	-5/12

TABLE 36--Continued

Γ_8^C					
j	k	ζ	j	k	ζ
1	5	$\sqrt{35}/10$	3	6	$-5/2\sqrt{42}$
1	6	$3/\sqrt{10}$	3	7	$3i\sqrt{14}/20$
1	10	$-3/2\sqrt{6}$	3	8	$-\sqrt{15}/6$
1	11	$\sqrt{14}/4$	3	9	$\sqrt{21}/10$
1	12	$-i/\sqrt{2}$	3	12	$-i\sqrt{210}/28$
1	16	$-2i/\sqrt{5}$	3	13	$9/10\sqrt{6}$
1	17	$-2i/\sqrt{5}$	3	14	$-i\sqrt{21}/5$
1	18	$3i/2\sqrt{5}$	3	18	$-5i/\sqrt{84}$
1	19	$3i/2\sqrt{5}$	3	19	$-5i/\sqrt{84}$
1	20	$1/2$	3	20	$\sqrt{105}/14$
1	21	$1/2$	3	21	$\sqrt{105}/14$
2	5	$-9/\sqrt{60}$	4	7	$-3/5$
2	6	$3/\sqrt{210}$	4	9	$i\sqrt{6}/5$
2	10	$\sqrt{14}/4$	4	13	$-i\sqrt{21}/5$
2	11	$1/2\sqrt{6}$	4	14	$-\sqrt{6}/10$
2	12	$-i/\sqrt{42}$	5	5	$1/3$
2	18	$-i\sqrt{105}/14$	5	10	$\sqrt{210}/20$
2	19	$-i\sqrt{105}/14$	5	11	$-9/\sqrt{40}$
2	20	$-5/\sqrt{84}$	5	16	$-i\sqrt{7}/3$
2	21	$-5/\sqrt{84}$	5	17	$14i/3\sqrt{7}$

TABLE 36--Continued

j	k	ζ	j	k	ζ
6	6	$1/8$	9	9	$-11/80$
6	7	$5i\sqrt{3}/24$	9	13	$3\sqrt{14}/10$
6	10	$-3/\sqrt{15}$	9	14	$3i/40$
6	11	$-1/\sqrt{35}$	10	10	$-1/4$
6	12	$-i\sqrt{5}/8$	10	11	$\sqrt{21}/12$
6	13	$5/8\sqrt{7}$	10	12	$i/\sqrt{3}$
6	18	$-i\sqrt{2}/8$	10	15	$-i/\sqrt{2}$
6	19	$i/\sqrt{8}$	10	16	$i\sqrt{30}/5$
6	20	$\sqrt{10}/8$	10	18	$i\sqrt{30}/10$
7	7	$3/40$	10	20	$-1/\sqrt{6}$
7	8	$7i/\sqrt{210}$	10	21	$2/\sqrt{6}$
7	9	$i\sqrt{6}/10$	11	11	$1/12$
7	12	$\sqrt{15}/8$	11	12	$i/3\sqrt{7}$
7	13	$3i\sqrt{21}/40$	11	15	$5i/\sqrt{42}$
7	14	$-2\sqrt{6}/5$	11	18	$-5i/\sqrt{70}$
7	18	$5/4\sqrt{6}$	11	20	$5/3\sqrt{14}$
7	19	$-5/2\sqrt{6}$	11	21	$-10/3\sqrt{14}$
7	20	$-i\sqrt{30}/8$	12	12	$-1/24$
8	8	$3/16$	12	13	$-15i/8\sqrt{35}$
8	9	$3\sqrt{35}/80$	12	15	$-1/\sqrt{6}$
8	13	$-1/\sqrt{10}$	12	18	$-\sqrt{10}/8$
8	14	$-3i\sqrt{35}/40$	12	20	$i\sqrt{2}/24$

TABLE 36--Continued

j	k	ζ	j	k	ζ
12	21	$-i\sqrt{2}/12$	17	17	$-1/6$
13	13	$3/8$	18	18	$-1/2$
13	15	$15i/\sqrt{210}$	18	19	$-1/2$
13	18	$-5i/4\sqrt{14}$	18	21	$i\sqrt{5}/2$
13	20	$-15/4\sqrt{70}$	19	19	$1/4$
13	21	$15/2\sqrt{70}$	19	20	$i\sqrt{5}/2$
14	14	$-1/4$	19	21	$i\sqrt{5}/4$
15	20	$i/\sqrt{3}$	20	20	$1/6$
15	21	$-2i/\sqrt{3}$	20	21	$1/6$
16	16	$1/3$	21	21	$-1/12$
16	17	$1/3$			

TABLE 37

The Decomposition of the Cubic States (Spin-Orbit Included) When the Symmetry is Lowered to D_4'

State in O'	State in D_4'
Γ_{6a}	Γ_{6a}
Γ_{6b}	Γ_{6b}
Γ_{7a}	Γ_{7a}
Γ_{7b}	Γ_{7b}
Γ_{8a}	Γ_{6a}
Γ_{8b}	Γ_{6b}
Γ_{8c}	Γ_{7a}
Γ_{8d}	Γ_{7b}

The non-zero matrix elements (the H'_{jk}'s) for the axial ligand field perturbation of the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme are given in Table 38. The complete energy matrices for this coupling scheme can then be obtained by appropriately superimposing the spin-orbit matrices (Γ_6^C, Γ_7^C and Γ_8^C from Table 35) and the cubic matrices (from Table 19) onto Γ_6^Q and Γ_7^Q from Table 38.

Checking of the Weak Field Perturbation Matrices

When two coupling schemes for the same ligand field problem are known they can be checked one versus the other. This is done by finding the unitary transformation matrices which connect the wave functions of the two coupling schemes and then recalculating the matrix elements of one coupling scheme in terms of those of the other.

Suppose we find that the wave functions ψ_1' and ψ_2' in coupling scheme A are mixed in coupling scheme B in which we have the new wave functions ψ_1 and ψ_2. If only ψ_1' and ψ_2' of A are used in forming ψ_1 and ψ_2 of coupling scheme B then we can say that

$$\psi_1 = a\ \psi_1' + b\ \psi_2' \quad \text{and} \tag{86a}$$

$$\psi_2 = c\ \psi_1' + d\ \psi_2' \quad . \tag{86b}$$

Thus, the unitary transformation matrix which gives ψ_1 and ψ_2 of B in terms of the wave functions of A is

TABLE 38

a) Numbering of the Eigenvectors of the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme for the Axial Ligand Field Perturbation

Γ_6^Q

1 through 21 = 1 through 21 of Γ_{8a}^C

22 through 30 = 1 through 9 of Γ_6^C

Γ_7^Q

1 through 21 = 1 through 21 of Γ_{8c}^C

22 through 30 = 1 through 9 of Γ_7^C

b) The Non-Zero Matrix Elements (H'_{jk}'s) for the Axial Ligand Field Perturbation of the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme

Γ_6^Q

j	k	H'_{jk}	j	k	H'_{jk}
1	1	$Ds+3Dt$	3	3	$-(48Ds+235Dt)/210$
1	2	$\sqrt{21}(3Ds-5Dt)/7$	3	4	$-i\sqrt{14}(2Ds-15Dt)/10$
1	3	$\sqrt{105}(3Ds-5Dt)/21$	3	22	$-(24Ds-5Dt)/6\sqrt{35}$
1	22	$-(3Ds-5Dt)/\sqrt{3}$	4	4	$-2(3Ds-5Dt)/5$
2	2	$(3Ds-19Dt)/7$	4	22	$i(2Ds-15Dt)/\sqrt{10}$
2	3	$\sqrt{5}(Ds+10Dt)/7$	5	5	$-2Ds/5$
2	22	$-(Ds+10Dt)/\sqrt{7}$	5	6	$-(144Ds-1045Dt)/60\sqrt{14}$

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
5	7	$i\sqrt{42}Dt/8$	6	24	$(48Ds+25Dt)/60\sqrt{2}$
5	8	$19\sqrt{5}Dt/12$	6	25	$7iDt/4\sqrt{6}$
5	9	$\sqrt{7}Dt/4$	6	26	$-\sqrt{35}(24Ds-5Dt)/84$
5	10	$\sqrt{210}Ds/10$	6	27	$7Dt/12$
5	11	$-Ds/\sqrt{10}$	7	7	$-(48Ds+95Dt)/120$
5	12	$-i(16Ds+55Dt)/4\sqrt{70}$	7	8	$i\sqrt{210}Dt/24$
5	13	$3\sqrt{2}Dt/8$	7	9	$-i\sqrt{6}(8Ds-95Dt)/40$
5	14	$-i\sqrt{7}Dt/2$	7	10	$i\sqrt{5}(2Ds-Dt)/4$
5	23	$-\sqrt{8}Ds/5$	7	11	$i\sqrt{105}(Ds+3Dt)/42$
5	24	$-(144Ds-275Dt)/60\sqrt{7}$	7	12	$-(16Ds-15Dt)/8\sqrt{15}$
5	25	$-i\sqrt{21}Dt/4$	7	13	$-i\sqrt{21}(8Ds-25Dt)/280$
5	26	$5\sqrt{10}Dt/12$	7	14	$\sqrt{6}(4Ds+75Dt)/120$
5	27	$-\sqrt{14}Dt/4$	7	23	$i\sqrt{21}Dt/4$
6	6	$(48Ds+95Dt)/120$	7	24	$-7iDt/4\sqrt{6}$
6	7	$-7iDt/8\sqrt{3}$	7	25	$-\sqrt{2}(48Ds+25Dt)/120$
6	8	$-5(24Ds-19Dt)/12\sqrt{70}$	7	26	$-i\sqrt{105}Dt/12$
6	9	$-7\sqrt{2}Dt/24$	7	27	$-i\sqrt{3}(8Ds-25Dt)/20$
6	10	$(6Ds+25Dt)/4\sqrt{15}$	8	8	$(12Ds-19Dt)/12$
6	11	$(27Ds+25Dt)/6\sqrt{35}$	8	9	$-\sqrt{35}Dt/12$
6	12	$-i(24Ds-5Dt)/24\sqrt{5}$	8	10	$35Dt/4\sqrt{42}$
6	13	$(16Ds+13Dt)/8\sqrt{7}$	8	11	$-5Dt/12\sqrt{2}$
6	14	$-i\sqrt{2}(12Ds+Dt)/24$	8	12	$-i(3Ds-5Dt)/3\sqrt{14}$
6	23	$-(144Ds-275Dt)/60\sqrt{7}$	8	13	$-(2Ds+5Dt)/\sqrt{40}$

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
8	14	$-i\sqrt{35}(12Ds+5Dt)/60$	10	24	$-(6Ds+25Dt)/2\sqrt{30}$
8	23	$5\sqrt{10}Dt/12$	10	25	$i\sqrt{10}(2Ds-Dt)/4$
8	24	$-\sqrt{35}(24Ds-5Dt)/84$	10	26	$-5\sqrt{21}Dt/12$
8	25	$i\sqrt{105}Dt/12$	10	27	$-7\sqrt{15}Dt/12$
8	26	$\sqrt{2}(12Ds-5Dt)/12$	11	11	$(9Ds+76Dt)/42$
8	27	$\sqrt{70}Dt/12$	11	12	$-i(27Ds+25Dt)/6\sqrt{7}$
9	9	$-(36Ds-95Dt)/60$	11	13	$-\sqrt{5}(Ds+3Dt)/14$
9	10	$35Dt/4\sqrt{30}$	11	14	$i\sqrt{70}Dt/12$
9	11	$-\sqrt{70}Dt/24$	11	23	$Ds/\sqrt{5}$
9	12	$-i(18Ds+5Dt)/6\sqrt{10}$	11	24	$-(27Ds+25Dt)/3\sqrt{70}$
9	13	$\sqrt{14}Ds/10$	11	25	$5i(Ds+3Dt)/\sqrt{210}$
9	14	$-i(36Ds-25Dt)/60$	11	26	$5Dt/12$
9	23	$-\sqrt{14}Dt/4$	11	27	$\sqrt{35}Dt/12$
9	24	$7Dt/12$	12	12	$7Dt/24$
9	25	$i\sqrt{3}(8Ds-25Dt)/20$	12	13	$-i(32Ds+75Dt)/8\sqrt{35}$
9	26	$\sqrt{70}Dt/12$	12	14	$(36Ds-25Dt)/12\sqrt{10}$
9	27	$-(36Ds-25Dt)/30\sqrt{2}$	12	23	$-i(16Ds+55Dt)/4\sqrt{35}$
10	10	$(Ds-4Dt)/2$	12	24	$-i(24Ds-5Dt)/12\sqrt{10}$
10	11	$(9Ds+20Dt)/\sqrt{84}$	12	25	$(16Ds-15Dt)/4\sqrt{30}$
10	12	$-i(6Ds+25Dt)/4\sqrt{3}$	12	26	$-i(3Ds-5Dt)/3\sqrt{7}$
10	13	$-\sqrt{105}(2Ds-Dt)/28$	12	27	$-i(18Ds+5Dt)/6\sqrt{5}$
10	14	$-35iDt/2\sqrt{30}$	13	13	$-(32Ds-345Dt)/280$
10	23	$-\sqrt{105}Ds/5$	13	14	$i\sqrt{14}(4Ds+15Dt)/40$

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
13	23	-3Dt/4	17	29	-(36Ds-25Dt)/30
13	24	-(16Ds+13Dt)/4√14	17	30	i(4Ds+5Dt)/2√5
13	25	-i√42(8Ds-25Dt)/280	18	18	7Dt/2
13	26	(2Ds+5Dt)/2√5	18	19	-(8Ds-25Dt)/20
13	27	-√7Ds/5	18	21	i√5(4Ds+5Dt)/20
14	14	-(9Ds+20Dt)/15	18	28	-(36Ds-25Dt)/30
14	23	-i√14Dt/2	18	29	(8Ds-25Dt)/20
14	24	-i(12Ds+Dt)/12	18	30	-i(4Ds+5Dt)/4√5
14	25	-√3(4Ds+75Dt)/60	19	19	7Dt/2
14	26	-i√70(12Ds+5Dt)/60	19	20	i(4Ds+5Dt)/4√5
14	27	-i(36Ds-25Dt)/30√2	19	28	-(36Ds-25Dt)/30
15	15	-7Dt	19	29	(8Ds-25Dt)/20
16	17	7Ds/5	19	30	i(4Ds+5Dt)/4√5
16	18	-7Dt/3	20	20	-7Dt/6
16	19	(36Ds-25Dt)/30	20	21	35Dt/12
16	21	i√5(4Ds+5Dt)/10	20	28	-i(4Ds+5Dt)/2√5
16	28	-7Ds/5	20	29	-i(4Ds+5Dt)/4√5
16	29	-(36Ds-25Dt)/30	20	30	35Dt/12
16	30	-i(4Ds+5Dt)/2√5	21	21	-7Dt/6
17	18	(36Ds-25Dt)/30	21	28	-i(4Ds+5Dt)/2√5
17	19	-7Dt/3	21	29	-i(4Ds+5Dt)/4√5
17	20	i(4Ds+5Dt)/2√5	21	30	-35Dt/12
17	28	-7Ds/5	22	22	-7Dt/6

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
23	24	$77Dt/6\sqrt{14}$	25	26	$i\sqrt{210}Dt/12$
23	25	$i\sqrt{42}Dt/4$	25	27	$21iDt/2\sqrt{6}$
23	26	$35Dt/6\sqrt{5}$	26	26	$-7Dt/6$
23	27	$\sqrt{7}Dt/2$	26	27	$-\sqrt{35}Dt/6$
24	24	$7Dt/12$	27	27	$7Dt/6$
24	25	$-7iDt/4\sqrt{3}$	28	29	$-7Dt/3$
24	26	$\sqrt{70}Dt/12$	29	29	$7Dt/2$
24	27	$-7\sqrt{2}Dt/12$	30	30	$-7Dt/6$
25	25	$-7Dt/12$			
		Γ_7^Q			
1	1	$-(2Ds-Dt/2$	4	4	$(18Ds+5Dt)/15$
1	2	$-(18Ds+5Dt)/\sqrt{84}$	4	22	$(18Ds+5Dt)/\sqrt{90}$
1	3	$-\sqrt{105}(Ds+3Dt)/7$	5	5	$2Ds/5$
1	4	$-35iDt/\sqrt{30}$	5	6	$3(16Ds+55Dt)/20\sqrt{14}$
1	22	$-i(3Ds-5Dt)/\sqrt{3}$	5	7	$3i\sqrt{42}Dt/8$
2	2	$-(18Ds+19Dt)/42$	5	8	$15Dt/4\sqrt{5}$
2	3	$-\sqrt{5}(Ds-18Dt)/7$	5	9	$3\sqrt{7}Dt/4$
2	4	$i\sqrt{70}Dt/6$	5	10	$-\sqrt{210}Ds/10$
2	22	$-i(27Ds-10Dt)/3\sqrt{7}$	5	11	$Ds/\sqrt{10}$
3	3	$(16Ds+55Dt)/70$	5	12	$i(16Ds+55Dt)/4\sqrt{70}$
3	4	$i\sqrt{14}(2Ds+15Dt)/10$	5	13	$-3Dt/4\sqrt{2}$
3	22	$-i(16Ds-15Dt)/2\sqrt{35}$	5	14	$i\sqrt{7}Dt/2$

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
5	23	$21Ds/\sqrt{105}$	7	11	$-i\sqrt{105}(Ds+3Dt)/42$
5	24	$-Ds/\sqrt{5}$	7	12	$(16Ds-15Dt)/8\sqrt{15}$
5	25	$-i(16Ds+55Dt)/4\sqrt{35}$	7	13	$i\sqrt{21}(8Ds-25Dt)/280$
5	26	$3Dt/4$	7	14	$-\sqrt{6}(4Ds+75Dt)/120$
5	27	$-7iDt/\sqrt{14}$	7	23	$i\sqrt{10}(2Ds-Dt)/4$
6	6	$-(16Ds-15Dt)/40$	7	24	$5i(Ds+3Dt)/\sqrt{210}$
6	7	$-7i\sqrt{3}Dt/8$	7	25	$-(16Ds-15Dt)/4\sqrt{30}$
6	8	$\sqrt{70}(8Ds+3Dt)/56$	7	26	$-i\sqrt{42}(8Ds-25Dt)/280$
6	9	$-7\sqrt{2}Dt/8$	7	27	$\sqrt{3}(4Ds+75Dt)/60$
6	10	$-(6Ds+25Dt)/4\sqrt{15}$	8	8	$-(4Ds+3Dt)/4$
6	11	$-(27Ds+25Dt)/6\sqrt{35}$	8	9	$-\sqrt{35}Dt/4$
6	12	$i(24Ds-5Dt)/24\sqrt{5}$	8	10	$-35Dt/4\sqrt{42}$
6	13	$-(16Ds+13Dt)/8\sqrt{7}$	8	11	$5\sqrt{2}Dt/24$
6	14	$i\sqrt{2}(12Ds+Dt)/24$	8	12	$i(3Ds-5Dt)/3\sqrt{14}$
6	23	$(6Ds+25Dt)/2\sqrt{30}$	8	13	$(2Ds+5Dt)/\sqrt{40}$
6	24	$(27Ds+25Dt)/3\sqrt{70}$	8	14	$i\sqrt{35}(12Ds+5Dt)/60$
6	25	$-i(24Ds-5Dt)/12\sqrt{10}$	8	23	$35Dt/4\sqrt{21}$
6	26	$(16Ds+13Dt)/4\sqrt{14}$	8	24	$-5Dt/12$
6	27	$-i(12Ds+Dt)/12$	8	25	$-i(3Ds-5Dt)/3\sqrt{7}$
7	7	$(16Ds-15Dt)/40$	8	26	$-(2Ds+5Dt)/2\sqrt{5}$
7	8	$i\sqrt{210}Dt/8$	8	27	$-i\sqrt{70}(12Ds+5Dt)/60$
7	9	$i\sqrt{6}(8Ds+45Dt)/40$	9	9	$3(4Ds+5Dt)/20$
7	10	$-i\sqrt{5}(2Ds-Dt)/4$	9	10	$-35Dt/4\sqrt{30}$

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
9	11	$\sqrt{70}Dt/24$	11	23	$-(27Ds+25Dt)/3\sqrt{42}$
9	12	$i(18Ds+5Dt)/6\sqrt{10}$	11	24	$-(27Ds+95Dt)/63\sqrt{2}$
9	13	$-\sqrt{14}Ds/10$	11	25	$i(81Ds+5Dt)/9\sqrt{14}$
9	14	$i(36Ds-25Dt)/60$	11	26	$\sqrt{10}(Ds-11Dt)/14$
9	23	$35Dt/4\sqrt{15}$	11	27	$i\sqrt{35}Dt/18$
9	24	$-\sqrt{35}Dt/12$	12	12	$-49Dt/72$
9	25	$-i(18Ds+5Dt)/6\sqrt{5}$	12	13	$i(32Ds-65Dt)/8\sqrt{35}$
9	26	$\sqrt{7}Ds/5$	12	14	$-(108Ds+65Dt)/36\sqrt{10}$
9	27	$-i(36Ds-25Dt)/30\sqrt{2}$	12	23	$-i(18Ds+5Dt)/6\sqrt{6}$
10	10	$-(3Ds+2Dt)/6$	12	24	$-i(81Ds+5Dt)/9\sqrt{14}$
10	11	$-(27Ds-10Dt)/6\sqrt{21}$	12	25	$-35\sqrt{2}Dt/72$
10	12	$i(18Ds-65Dt)/12\sqrt{3}$	12	26	$i(32Ds+5Dt)/4\sqrt{70}$
10	13	$\sqrt{105}(6Ds+25Dt)/84$	12	27	$-(108Ds-5Dt)/36\sqrt{5}$
10	14	$-175iDt/6\sqrt{30}$	13	13	$(96Ds+785Dt)/840$
10	23	$-(3Ds-5Dt)/3\sqrt{2}$	13	14	$-i(28Ds+245Dt)/20\sqrt{14}$
10	24	$-(27Ds+25Dt)/3\sqrt{42}$	13	23	$\sqrt{210}(6Ds+11Dt)/84$
10	25	$i(18Ds+5Dt)/6\sqrt{6}$	13	24	$\sqrt{10}(Ds-11Dt)/14$
10	26	$\sqrt{210}(6Ds+11Dt)/84$	13	25	$-i(32Ds+5Dt)/4\sqrt{70}$
10	27	$-35iDt/6\sqrt{15}$	13	26	$\sqrt{2}(96Ds-125Dt)/840$
11	11	$-(27Ds-38Dt)/126$	13	27	$-i\sqrt{7}(4Ds+25Dt)/20$
11	12	$i(81Ds-65Dt)/18\sqrt{7}$	14	14	$(27Ds-10Dt)/45$
11	13	$\sqrt{5}(Ds-25Dt)/14$	14	23	$35iDt/6\sqrt{15}$
11	14	$5i\sqrt{70}Dt/36$	14	24	$-i\sqrt{35}Dt/18$

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
14	25	$-(108Ds-5Dt)/36\sqrt{5}$	19	19	$7Dt/2$
14	26	$i\sqrt{7}(4Ds+25Dt)/20$	19	20	$-i(4Ds+5Dt)/4\sqrt{5}$
14	27	$\sqrt{2}(27Ds+25Dt)/45$	19	28	$(36Ds-25Dt)/30$
15	15	$-7Dt$	19	29	$-(8Ds-25Dt)/20$
16	17	$-7Ds/5$	19	30	$i(4Ds+5Dt)/4\sqrt{5}$
16	18	$-7Dt/3$	20	20	$-7Dt/6$
16	19	$-(36Ds-25Dt)/30$	20	21	$-35Dt/12$
16	21	$-i(4Ds+5Dt)/2\sqrt{5}$	20	28	$-i(4Ds+5Dt)/2\sqrt{5}$
16	28	$-7Ds/5$	20	29	$-i(4Ds+5Dt)/4\sqrt{5}$
16	29	$-(36Ds-25Dt)/30$	20	30	$-35Dt/12$
16	30	$i(4Ds+5Dt)/2\sqrt{5}$	21	21	$-7Dt/6$
17	18	$-(36Ds-25Dt)/30$	21	28	$i(4Ds+5Dt)/2\sqrt{5}$
17	19	$-7Dt/3$	21	29	$i(4Ds+5Dt)/4\sqrt{5}$
17	20	$-i(4Ds+5Dt)/2\sqrt{5}$	21	30	$-35Dt/12$
17	28	$7Ds/5$	22	22	$-7Dt/6$
17	29	$(36Ds-25Dt)/30$	23	23	$-7Dt/6$
17	30	$i(4Ds+5Dt)/2\sqrt{5}$	23	24	$35Dt/6\sqrt{21}$
18	18	$7Dt/2$	23	25	$-35iDt/6\sqrt{3}$
18	19	$(8Ds-25Dt)/20$	23	26	$\sqrt{105}Dt/6$
18	21	$-i(4Ds+5Dt)/4\sqrt{5}$	23	27	$-70iDt/3\sqrt{30}$
18	28	$-(36Ds-25Dt)/30$	24	24	$19Dt/18$
18	29	$(8Ds-25Dt)/20$	24	25	$-35iDt/9\sqrt{7}$
18	30	$i(4Ds+5Dt)/4\sqrt{5}$	24	26	$-\sqrt{5}Dt$

TABLE 38--Continued

j	k	H'_{jk}	j	k	H'_{jk}
24	27	$i\sqrt{70}Dt/9$	26	27	$-i\sqrt{14}Dt/4$
25	25	$-7Dt/36$	27	27	$-7Dt/9$
25	26	$-i\sqrt{35}Dt/4$	28	29	$-7Dt/3$
25	27	$-35Dt/18\sqrt{10}$	29	29	$7Dt/2$
26	26	$13Dt/12$	30	30	$-7Dt/6$

$$\begin{array}{c||cc||} & \psi_1' & \psi_2' \\ \psi_1 & a & b \\ \psi_2 & c & d \end{array} \tag{87}$$

The coefficients a, b, c and d are determined as follows. If ψ_1 is, in terms of the basis vectors ψ_1^o and ψ_2^o,

$$\psi_1 = p\,\psi_1^o + q\,\psi_2^o \tag{88}$$

then

$$\psi_1' = p'\,\psi_1^o + q'\,\psi_2^o \quad \text{and} \tag{89a}$$

$$\psi_2' = p''\,\psi_1^o + q''\,\psi_2^o \quad . \tag{89b}$$

Substituting (88), (89a) and (89b) into (86a) we obtain

$$p\psi_1^o + q\psi_2^o = a(p'\psi_1^o + q'\psi_2^o) + b(p''\psi_1^o + q''\psi_2^o) \tag{90}$$

and hence,

$$p = ap' + bp'' \quad \text{and} \tag{91a}$$

$$q = aq' + bq'' \quad . \tag{91b}$$

The coefficients p, q, p', q', p'' and q'' are taken from the wave functions of the two coupling schemes. Therefore, we have two equations and two unkowns and we can easily calculate a and b. A similar procedure yields c and d.

Suppose we wish to obtain the matrix elements in scheme B knowing the matrix elements in scheme A and the unitary transformation matrices. The calculations are done as follows. The matrix elements are given by, for example,

$$H_{11}' = \int \psi_1'^{*} H' \psi_1 \, d\tau \, .$$

Substituting the identity $\psi_1 = a\,\psi_1' + b\,\psi_2'$ yields

$$H_{11}' = \int (a\psi_1' + b\psi_2')^{*} H' (a\psi_1' + b\psi_2') \, d\tau \quad .$$

This reduces to

$$H_{11}' = a^{*} a \int \psi_1'^{*} H' \psi_1' d\tau + a^{*} b \int \psi_1'^{*} H' \psi_2' d\tau$$

$$+ b^{*} a \int \psi_2'^{*} H' \psi_1' d\tau + b^{*} b \int \psi_2'^{*} H' \psi_2' d\tau \, .$$

Since we know the matrix elements of coupling scheme A and the coefficients from the unitary transformation matrix, H_{11}' can be calculated.

In general the perturbation matrices of coupling scheme B, which we will call H_B, are given by

$$H_B = T(\Gamma_j)^{*} H_A T(\Gamma_j) \qquad (92)$$

hwere H_A is the corresponding perturbation matrix of scheme A and $T(\Gamma_j)$ is the unitary transformation matrix between B and A for the j^{th} irreducible representation.

Thus, we have a sound procedure for verifying the calculations in one coupling scheme when calculations in a second scheme are available for the same electronic configuration and geometry.

We have obtained the unitary transformation matrix between the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme and the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme. The elements of this unitary transformation matrix are presented in Table 39.

We have checked the matrix elements of these two weak field coupling schemes using this unitary transformation matrix.

Making use of a diagonalization computer program we have compared the eigenvalues obtained from the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ coupling scheme with those obtained from the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme. For all identical sets of parameters tested the two weak field coupling schemes yield identical eigenvalues. This is proof that the energy matrices are correct in both coupling schemes.

TABLE 39

The Elements of the Unitary Transformation Matrix Between the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme and the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme

---

The numbering of the eigenvectors used below is consistent with Tables 36 and 38 for $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ and with Table 28 for $\{L,S,X^C,X^Q,\Gamma^Q\}$. The general form used below is

$$(\{L,S,X^C,\Gamma^C,\Gamma^Q\}) = \sum_i C_i \cdot (\{L,S,X^C,X^Q,\Gamma^Q\})$$

where C_i is the appropriate constant.

Γ_6^Q

---

(1) = -(1)

(2) = -(2)

(3) = -(4)

(4) = -(5)

(5) = $(-\sqrt{6}/3)(6)-(\sqrt{3}/3)(11)$

(6) = $(-\sqrt{6}/3)(7)-(\sqrt{3}/3)(14)$

(7) = $(-\sqrt{6}/3)(8)-(\sqrt{3}/3)(16)$

(8) = $(-\sqrt{6}/3)(9)-(\sqrt{3}/3)(19)$

(9) = $(-\sqrt{6}/3)(10)-(\sqrt{3}/3)(20)$

(10) = -i(12)

(11) = -i(13)

(12) = -i(15)

(13) = -i(17)

(14) = -i(18)

TABLE 39--Continued

$(15) = (23)$

$(16) = i(\sqrt{3}/3)(21)+i(\sqrt{6}/3)(25)$

$(17) = i(\sqrt{3}/3)(21)-i(\sqrt{6}/6)(25)+(\sqrt{2}/2)(26)$

$(18) = i(\sqrt{3}/3)(22)+i(\sqrt{6}/3)(27)$

$(19) = i(\sqrt{3}/3)(22)-i(\sqrt{6}/6)(27)+(\sqrt{2}/2)(28)$

$(20) = (\sqrt{3}/3)(24)+i(\sqrt{6}/3)(30)$

$(21) = -(\sqrt{3}/3)(24)-(\sqrt{2}/2)(29)+i(\sqrt{6}/6)(30)$

$(22) = (3)$

$(23) = -(\sqrt{3}/3)(6)+(\sqrt{6}/3)(11)$

$(24) = -(\sqrt{3}/3)(7)+(\sqrt{6}/3)(14)$

$(25) = -(\sqrt{3}/3)(8)+(\sqrt{6}/3)(16)$

$(26) = -(\sqrt{3}/3)(9)+(\sqrt{6}/3)(19)$

$(27) = -(\sqrt{3}/3)(10)+(\sqrt{6}/3)(20)$

$(28) = -i(\sqrt{3}/3)(21)+i(\sqrt{6}/6)(25)+(\sqrt{2}/2)(26)$

$(29) = -i(\sqrt{3}/3)(22)+i(\sqrt{6}/6)(27)+(\sqrt{2}/2)(28)$

$(30) = -(\sqrt{3}/3)(24)+(\sqrt{2}/2)(29)+i(\sqrt{6}/6)(30)$

$\Gamma_7{}^Q$

$(1) = -(1)$

$(2) = -(2)$

$(3) = -(4)$

$(4) = -(5)$

$(5) = (6)$

$(6) = (7)$

TABLE 39--Continued

$(7) = (8)$

$(8) = (9)$

$(9) = (10)$

$(10) = -i(\sqrt{3}/3)(11)-i(\sqrt{6}/3)(19)$

$(11) = -i(\sqrt{3}/3)(12)-i(\sqrt{6}/3)(20)$

$(12) = -i(\sqrt{3}/3)(13)-i(\sqrt{6}/3)(16)$

$(13) = -i(\sqrt{3}/3)(14)-i(\sqrt{6}/3)(18)$

$(14) = -i(\sqrt{3}/3)(15)-i(\sqrt{6}/3)(17)$

$(15) = -(23)$

$(16) = -i(\sqrt{3}/3)(21)-i(\sqrt{6}/3)(26)$

$(17) = i(\sqrt{3}/3)(21)+i(\sqrt{2}/2)(25)-i(\sqrt{6}/6)(26)$

$(18) = -i(\sqrt{3}/3)(22)-i(\sqrt{6}/3)(28)$

$(19) = i(\sqrt{3}/3)(22)+i(\sqrt{2}/2)(27)-i(\sqrt{6}/6)(28)$

$(20) = (\sqrt{3}/3)(24)+(\sqrt{6}/3)(29)$

$(21) = (\sqrt{3}/3)(24)-(\sqrt{6}/6)(29)-(\sqrt{2}/2)(30)$

$(22) = -(3)$

$(23) = i(\sqrt{6}/3)(11)-i(\sqrt{3}/3)(19)$

$(24) = i(\sqrt{6}/3)(12)-i(\sqrt{3}/3)(20)$

$(25) = i(\sqrt{6}/3)(13)-i(\sqrt{3}/3)(16)$

$(26) = i(\sqrt{6}/3)(14)-i(\sqrt{3}/3)(18)$

$(27) = i(\sqrt{6}/3)(15)-i(\sqrt{3}/3)(17)$

$(28) = i(\sqrt{3}/3)(21)-i(\sqrt{2}/2)(25)-i(\sqrt{6}/6)(26)$

$(29) = i(\sqrt{3}/3)(22)-i(\sqrt{2}/2)(27)-i(\sqrt{6}/6)(28)$

$(30) = (\sqrt{3}/3)(24)-(\sqrt{6}/6)(29)+(\sqrt{2}/2)(30)$

CHAPTER III

THE STRONG FIELD COUPLING SCHEME

For the strong field case the first perturbation considered is the cubic ligand field potential. In this particular coupling scheme for d^3 the perturbations are considered in the following sequence:

$$V_c, \text{ then } e^2/r_{ij}, \text{ then } \xi(r)\vec{\ell}\cdot\vec{s}, \text{ then } V_a.$$

The Cubic Ligand Field

The five d orbitals, for which $\ell = 2$, are split in a cubic (O_h) field exactly as a D term is (cf. Table 10). Thus, the single electron d orbitals yield e_g and t_{2g} in a cubic field. This splitting is illustrated in Fig. 10.

The magnitude of the splitting of the single electron d orbitals is given by the well-known cubic ligand field parameter Δ, Δ being equal to 10 Dq. The t_{2g} orbitals have an energy of $-4Dq$ relative to the unperturbed d orbital set while the e_g orbitals have a relative energy of $+6Dq$.

For d^3 the electrons may be distributed into the t_{2g} and e_g orbitals to yield the following configurations: $(t_{2g})^3$, $(t_{2g})^2e_g$, $t_{2g}(e_g)^2$ and $(e_g)^3$.

The energy of each of these configurations is then readily calculated using the splitting given in Fig. 10. The energies for the

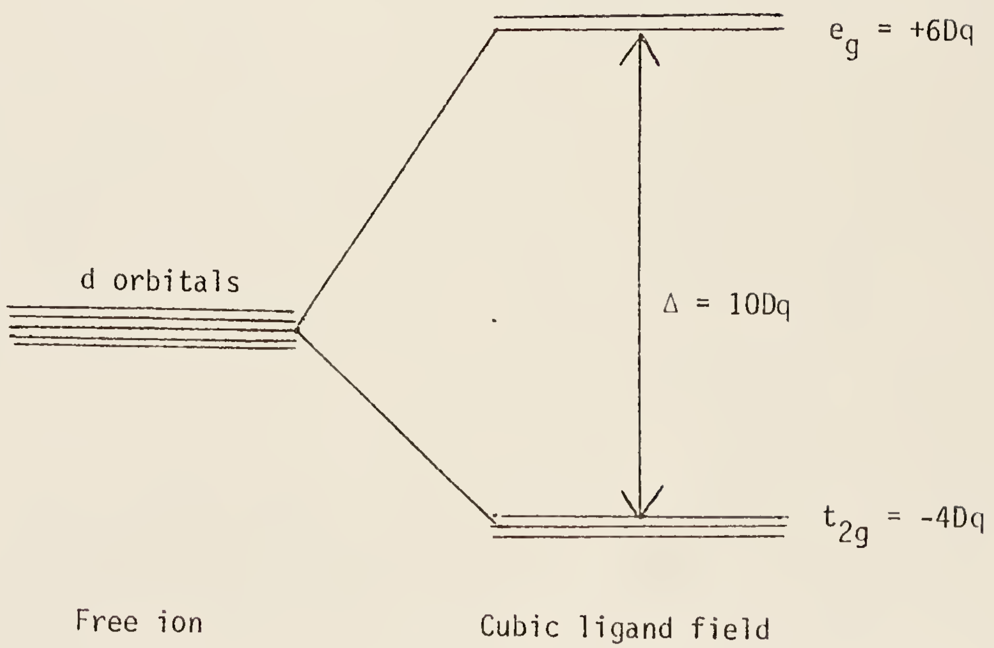

Figure 10. The Splitting of the Single Electron d orbitals in a Cubic Ligand Field.

cubic ligand field perturbation for this, and all other, strong field coupling scheme are

$$(t_{2g})^3 = -12Dq \tag{93a}$$

$$(t_{2g})^2e_g = -2Dq \tag{93b}$$

$$t_{2g}(e_g)^2 = 8Dq \tag{93c}$$

$$(e_g)^3 = 18Dq \tag{93d}$$

The weak field wave functions were composed of the three electron m_ℓ and m_s microstates. The d^3 strong field microstates are formed using the real forms of the single electron d orbitals: (xy), (yz), (xz), (x^2-y^2) and (z^2). The linear combinations of (m_ℓ) which correspond to these real forms of the d orbitals are given below.

$$(xy) = i((-2)-(2))/\sqrt{2} \tag{94a}$$

$$(yz) = i((-1)+(1))/\sqrt{2} \tag{94b}$$

$$(xz) = ((-1)-(1))/\sqrt{2} \tag{94c}$$

$$(x^2-y^2) = ((-2)+(2))/\sqrt{2} \tag{94d}$$

$$(z^2) = (0) \tag{94e}$$

From Table 15 we see that (z^2) is a basis for e_{ga}, (x^2-y^2) is a basis for e_{gb}, (xy) is a basis for t_{2ga}, (xz) is a basis for t_{2gb}, and (yz) is a basis for t_{2gc}. Thus, one microstate for $(t_{2g})^3$ is $|(xy)(xz)(yz)|$, another is $|(xy)(\overline{xy})(xz)|$. One microstate for $(t_{2g})^2e_g$ is $|(xy)(yz)(z^2)|$. Continuing on in this straightforward fashion we can write down all the possible strong field microstates for the four configurations; $(t_{2g})^3$, $(t_{2g})^2e_g$, $t_{2g}(e_g)^2$ and $(e_g)^3$. This is the strong field microstate table for d^3 and it is given in Table 40.

The Interelectronic Repulsions

We must now determine how the strong field configurations $(t_{2g})^3$, $(t_{2g})^2e_g$, $t_{2g}(e_g)^2$ and $(e_g)^3$ are split when the interelectronic repulsion perturbation is considered.

Let us begin with $(t_{2g})^3$. This configuration can be considered to be $(t_{2g})^2t_{2g}$. Thus, the direct product $(t_{2g})^2$ must be analyzed first.

Using the character table for O' (Table 31a) we find that $(t_{2g})^2$ decomposes as follows

$$(t_{2g})^2 = A_{1g}+E_g+T_{1g}+T_{2g} \tag{95a}$$

To determine the spin multiplicities of the states which $(t_{2g})^2$ yields, (95a), we must consider the total multiplicity of $(t_{2g})^2$, which is 15, and the correlation diagram between the strong and weak field coupling schemes for d^2, (cf. Cotton[1]). This yields the following result

---

[1] F. A. Cotton, Chemical Applications of Group Theory, 2nd ed., Wiley-Interscience, New York, 1971.

TABLE 40

The Strong Field Microstate Table for d^3

	$(t_{2g})^3$	
$\lvert(xy)(\overline{xy})(xz)\rvert$	$\lvert(xz)(\overline{xz})(\overline{yz})\rvert$	$\lvert(\overline{xy})(xz)(yz)\rvert$
$\lvert(xy)(\overline{xy})(\overline{xz})\rvert$	$\lvert(yz)(\overline{yz})(xy)\rvert$	$\lvert(xy)(\overline{xz})(\overline{yz})\rvert$
$\lvert(xy)(\overline{xy})(yz)\rvert$	$\lvert(yz)(\overline{yz})(\overline{xy})\rvert$	$\lvert(\overline{xy})(xz)(\overline{yz})\rvert$
$\lvert(xy)(\overline{xy})(\overline{yz})\rvert$	$\lvert(yz)(\overline{yz})(xz)\rvert$	$\lvert(\overline{xy})(\overline{xz})(yz)\rvert$
$\lvert(xz)(\overline{xz})(xy)\rvert$	$\lvert(yz)(\overline{yz})(\overline{xz})\rvert$	$\lvert(\overline{xy})(\overline{xz})(\overline{yz})\rvert$
$\lvert(xz)(\overline{xz})(\overline{xy})\rvert$	$\lvert(xy)(xz)(\overline{yz})\rvert$	$\lvert(xy)(xz)(yz)\rvert$
$\lvert(xz)(\overline{xz})(yz)\rvert$	$\lvert(xy)(\overline{xz})(yz)\rvert$	

	$(t_{2g})^2e_g$	
$\lvert(xy)(\overline{xy})(z^2)\rvert$	$\lvert(xy)(\overline{xz})(\overline{z^2})\rvert$	$\lvert(\overline{xy})(\overline{xz})(x^2-y^2)\rvert$
$\lvert(xy)(\overline{xy})(\overline{z^2})\rvert$	$\lvert(xy)(\overline{xz})(x^2-y^2)\rvert$	$\lvert(\overline{xy})(\overline{xz})(\overline{x^2-y^2})\rvert$
$\lvert(xy)(\overline{xy})(x^2-y^2)\rvert$	$\lvert(xy)(\overline{xz})(\overline{x^2-y^2})\rvert$	$\lvert(xy)(\overline{yz})(z^2)\rvert$
$\lvert(xy)(\overline{xy})(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xy})(xz)(z^2)\rvert$	$\lvert(xy)(\overline{yz})(\overline{z^2})\rvert$
$\lvert(xz)(\overline{xz})(z^2)\rvert$	$\lvert(\overline{xy})(xz)(\overline{z^2})\rvert$	$\lvert(xy)(\overline{yz})(x^2-y^2)\rvert$
$\lvert(xz)(\overline{xz})(\overline{z^2})\rvert$	$\lvert(\overline{xy})(xz)(x^2-y^2)\rvert$	$\lvert(xy)(\overline{yz})(\overline{x^2-y^2})\rvert$
$\lvert(xz)(\overline{xz})(x^2-y^2)\rvert$	$\lvert(\overline{xy})(xz)(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xy})(yz)(z^2)\rvert$
$\lvert(xz)(\overline{xz})(\overline{x^2-y^2})\rvert$	$\lvert(xy)(xz)(z^2)\rvert$	$\lvert(\overline{xy})(yz)(\overline{z^2})\rvert$
$\lvert(xz)(\overline{yz})(\overline{z^2})\rvert$	$\lvert(xy)(xz)(\overline{z^2})\rvert$	$\lvert(\overline{xy})(yz)(x^2-y^2)\rvert$
$\lvert(yz)(\overline{yz})(z^2)\rvert$	$\lvert(xy)(xz)(x^2-y^2)\rvert$	$\lvert(\overline{xy})(yz)(\overline{x^2-y^2})\rvert$
$\lvert(yz)(\overline{yz})(x^2-y^2)\rvert$	$\lvert(xy)(xz)(\overline{x^2-y^2})\rvert$	$\lvert(xy)(yz)(z^2)\rvert$
$\lvert(yz)(\overline{yz})(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xy})(\overline{xz})(z^2)\rvert$	$\lvert(xy)(yz)(\overline{z^2})\rvert$
$\lvert(xy)(\overline{xz})(z^2)\rvert$	$\lvert(\overline{xy})(\overline{xz})(\overline{z^2})\rvert$	$\lvert(xy)(yz)(x^2-y^2)\rvert$

TABLE 40--Continued

$\lvert(xy)(yz)(\overline{x^2-y^2})\rvert$	$\lvert(xz)(\overline{yz})(x^2-y^2)\rvert$	$\lvert(xz)(yz)(\overline{z^2})\rvert$
$\lvert(\overline{xy})(\overline{yz})(z^2)\rvert$	$\lvert(xz)(\overline{yz})(x^2-y^2)\rvert$	$\lvert(xz)(yz)(x^2-y^2)\rvert$
$\lvert(\overline{xy})(\overline{yz})(\overline{z^2})\rvert$	$\lvert(\overline{xz})(yz)(z^2)\rvert$	$\lvert(xz)(yz)(\overline{x^2-y^2})\rvert$
$\lvert(\overline{xy})(\overline{yz})(x^2-y^2)\rvert$	$\lvert(\overline{xz})(yz)(\overline{z^2})\rvert$	$\lvert(\overline{xz})(\overline{yz})(z^2)\rvert$
$\lvert(\overline{xy})(\overline{yz})(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xz})(yz)(x^2-y^2)\rvert$	$\lvert(\overline{xz})(\overline{yz})(\overline{z^2})\rvert$
$\lvert(xz)(\overline{yz})(z^2)\rvert$	$\lvert(\overline{xz})(yz)(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xz})(\overline{yz})(x^2-y^2)\rvert$
$\lvert(xz)(\overline{yz})(\overline{z^2})\rvert$	$\lvert(xz)(yz)(z^2)\rvert$	$\lvert(\overline{xz})(\overline{yz})(\overline{x^2-y^2})\rvert$

$t_{2g}(e_g)^2$

$\lvert(xy)(z^2)(\overline{z^2})\rvert$	$\lvert(xz)(z^2)(\overline{z^2})\rvert$	$\lvert(yz)(z^2)(\overline{z^2})\rvert$
$\lvert(\overline{xy})(z^2)(\overline{z^2})\rvert$	$\lvert(\overline{xz})(z^2)(\overline{z^2})\rvert$	$\lvert(\overline{yz})(z^2)(\overline{z^2})\rvert$
$\lvert(xy)(z^2)(x^2-y^2)\rvert$	$\lvert(xz)(z^2)(x^2-y^2)\rvert$	$\lvert(yz)(z^2)(x^2-y^2)\rvert$
$\lvert(xy)(z^2)(\overline{x^2-y^2})\rvert$	$\lvert(xz)(z^2)(\overline{x^2-y^2})\rvert$	$\lvert(yz)(z^2)(\overline{x^2-y^2})\rvert$
$\lvert(xy)(\overline{z^2})(x^2-y^2)\rvert$	$\lvert(xz)(\overline{z^2})(x^2-y^2)\rvert$	$\lvert(yz)(\overline{z^2})(x^2-y^2)\rvert$
$\lvert(xy)(z^2)(x^2-y^2)\rvert$	$\lvert(xz)(\overline{z^2})(\overline{x^2-y^2})\rvert$	$\lvert(yz)(\overline{z^2})(\overline{x^2-y^2})\rvert$
$\lvert(\overline{xy})(z^2)(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xz})(z^2)(x^2-y^2)\rvert$	$\lvert(\overline{yz})(z^2)(x^2-y^2)\rvert$
$\lvert(\overline{xy})(\overline{z^2})(x^2-y^2)\rvert$	$\lvert(\overline{xz})(z^2)(\overline{x^2-y^2})\rvert$	$\lvert(\overline{yz})(z^2)(\overline{x^2-y^2})\rvert$
$\lvert(\overline{xy})(\overline{z^2})(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xz})(\overline{z^2})(x^2-y^2)\rvert$	$\lvert(\overline{yz})(\overline{z^2})(x^2-y^2)\rvert$
$\lvert(\overline{xy})(\overline{z^2})(x^2-y^2)\rvert$	$\lvert(\overline{xz})(\overline{z^2})(\overline{x^2-y^2})\rvert$	$\lvert(\overline{yz})(z^2)(\overline{x^2-y^2})\rvert$
$\lvert(xy)(x^2-y^2)(\overline{x^2-y^2})\rvert$	$\lvert(\overline{xz})(x^2-y^2)(\overline{x^2-y^2})\rvert$	$\lvert(yz)(x^2-y^2)(\overline{x^2-y^2})\rvert$
$\lvert(\overline{xy})(x^2-y^2)(\overline{x^2-y^2})\rvert$	$\lvert(xz)(x^2-y^2)(\overline{x^2-y^2})\rvert$	$\lvert(\overline{yz})(x^2-y^2)(\overline{x^2-y^2})\rvert$

TABLE 40--Continued

$(e_g)^3$	
$\|(z^2)(\overline{z}^2)(x^2-y^2)\|$	$\|(z^2)(x^2-y^2)(x^2-\overline{y}^2)\|$
$\|(z^2)(\overline{z}^2)(x^2-\overline{y}^2)\|$	$\|(\overline{z}^2)(x^2-y^2)(x^2-\overline{y}^2)\|$

$$(t_{2g})^2 = {}^1A_{1g}+{}^1E_g+{}^3T_{1g}+{}^1T_{2g} \qquad (95b)$$

Now for the product $(t_{2g})^2t_{2g}$ we must consider only the state in $(t_{2g})^2$ with maximum spin multiplicity, i.e., ${}^3T_{1g}$. Thus, the direct product which will yield the states for $(t_{2g})^3$ is

$$(t_{2g})^2t_{2g} = {}^3T_{1g}xt_{2g} = A_{2g}+E_g+T_{1g}+T_{2g} \qquad (96a)$$

To determine the spin multiplicities of the states which $(t_{2g})^3$ yields, (96a), we need only consider the total multiplicity of $(t_{2g})^3$, which is 20. The multiplicity of 20 for $(t_{2g})^3$ can only be obtained by the following combination of spin multiplicities

$$(t_{2g})^3 = {}^4A_{2g}+{}^2E_g+{}^2T_{1g}+{}^2T_{2g} \qquad (96b)$$

For the configuration $(t_{2g})^2e_g$ we have the following direct product

$$(t_{2g})^2e_g = ({}^1A_{1g}+{}^1E_g+{}^3T_{1g}+{}^1T_{2g}) \times e_g \qquad (97a)$$

which yields

$$(t_{2g})^2e_g = {}^2A_{1g}+{}^2A_{2g}+2{}^2E_g+2{}^2T_{1g} + 2{}^2T_{2g}+{}^4T_{1g}+{}^4T_{2g} \quad . \qquad (97b)$$

For the configuration $t_{2g}(e_g)^2$ we must first analyze the product $(e_g)^2$. This product yields

$$(e_g)^2 = A_{1g}+A_{2g}+E_g \quad . \qquad (98a)$$

To determine the spin multiplicities of the states which $(e_g)^2$ yields, (98a), we must consider the total multiplicity of $(e_g)^2$, which is 6, and the correlation diagram between the strong and weak field coupling schemes for d^2, (cf. Cotton[1]). This yields the following result

$$(e_g)^2 = {}^1A_{1g} + {}^3A_{2g} + {}^1E_g \quad . \tag{98b}$$

Thus, for the configuration $t_{2g}(e_g)^2$ we have the following direct product.

$$t_{2g}(e_g)^2 = t_{2g} \times ({}^1A_{1g} + {}^3A_{2g} + {}^1E_g) \tag{99a}$$

which yields

$$t_{2g}(e_g)^2 = 2\,{}^2T_{1g} + 2\,{}^2T_{2g} + {}^4T_{1g} \quad . \tag{99b}$$

Lastly, for the configuration $(e_g)^3$ we must consider only ${}^1A_{1g}$ of $(e_g)^2$ in the product $(e_g)^2e_g$. Thus, the direct product which will yield the states for $(e_g)^3$ is

$$(e_g)^2e_g = {}^1A_{1g} \times e_g = {}^2E_g \tag{100}$$

A summary of these results for the decomposition of the strong field configurations when the interelectronic repulsion perturbation is considered is given in Table 41.

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[1] F. A. Cotton, Chemical Applications of Group Theory, 2nd ed., Wiley-Interscience, New York, 1971.

TABLE 41

The Splitting of the Strong Field Configurations of d^3 When the Interelectronic Repulsions Perturbation is Added

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$$(t_{2g})^3 = {}^2E_g + {}^2T_{1g} + {}^2T_{2g} + {}^4A_{2g}$$

$$(t_{2g})^2e_g = {}^2A_{1g} + {}^2A_{2g} + 2\,{}^2E_g + 2\,{}^2T_{1g} +$$

$$2\,{}^2T_{2g} + {}^4T_{1g} + {}^4T_{2g}$$

$$t_{2g}(e_g)^2 = 2\,{}^2T_{1g} + 2\,{}^2T_{2g} + {}^4T_{1g}$$

$$(e_g)^3 = {}^2E_g$$

To confirm that the decomposition of the strong field configurations has been carried out properly we have constructed the correlation diagram between the strong and weak field coupling schemes for d^3. This diagram, given as Fig. 11, is for the case of octahedral symmetry without the inclusion of the spin-orbit interaction.

To find the wave functions which correspond to the interelectronic repulsion states we must find which strong field microstate (or linear combination of microstates) transforms as the irreducible representation to which the state belongs.

These combinations for the various states are given in Table 42.[1]

To calculate the interelectronic repulsion energies we can proceed as follows. Using the (m_ℓ) combinations which correspond to the real forms of the d orbitals, (cf. equations 94a-e), we can convert the strong field microstates into weak field microstates. Then we can rewrite the strong field wave functions (cf. Table 42) in weak field microstate form and calculate the interelectronic repulsion energies, as multiples of the Racah parameters (A, B and C), exactly as we did for the weak field case.

Let us consider the a component of the ^2E_g state of $(e_g)^3$ as an illustration of the transformation from strong to weak field microstate form. From Table 42 we have

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[1] J. R. Perumareddi, Coordin. Chem. Rev., 4, 73(1969).

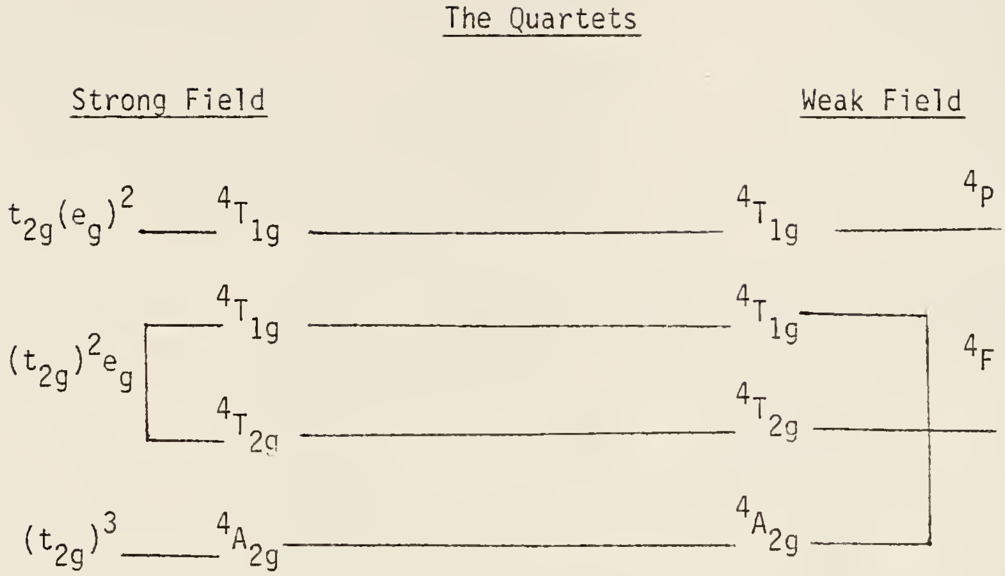

Figure 11. The d^3 Correlation Diagram Between the Strong Field and the Weak Field for the Case of O_h Symmetry Without the Inclusion of the Spin-Orbit Interaction.

The Doublets

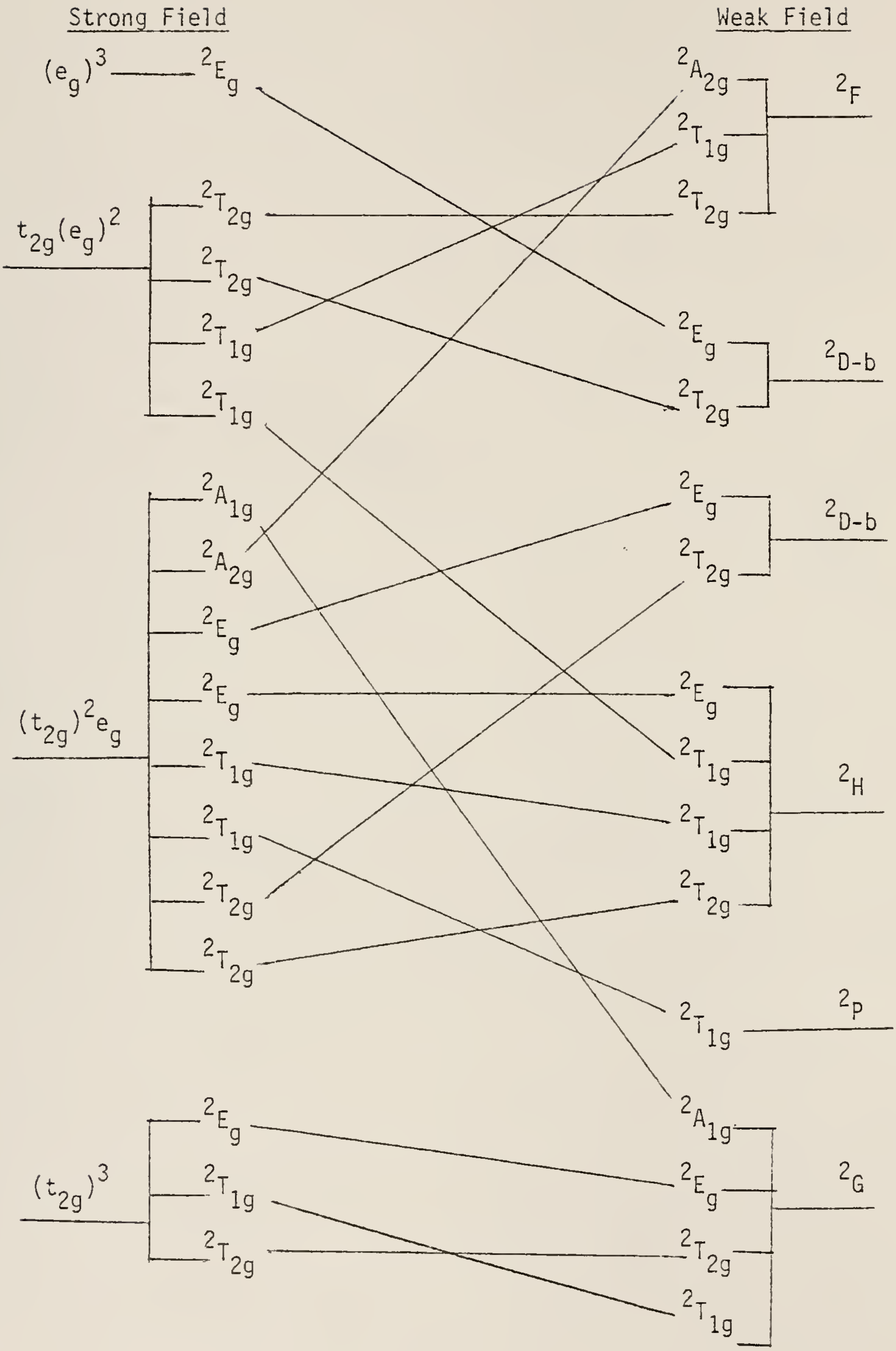

TABLE 42

The Symmetry Adapted Strong Field Wave Functions: Cubic Fields[k]

$$^{2}A_{1g}^{C}$$

$$(t_{2g})^{2}e_{g} = (-2|(xy)(\overline{xy})(z^{2})| + |(yz)(\overline{yz})(z^{2})| + |(xz)(\overline{xz})(z^{2})|$$
$$+\sqrt{3}|(xz)(\overline{xz})(x^{2}-y^{2})| - \sqrt{3}|(yz)(\overline{yz})(x^{2}-y^{2})|)/2\sqrt{3}$$

$$^{2}A_{2g}^{C}$$

$$(t_{2g})^{2}e_{g} = (-2|(xy)(\overline{xy})(x^{2}-y^{2})| + |(xz)(\overline{xz})(x^{2}-y^{2})|$$
$$+|(yz)(\overline{yz})(x^{2}-y^{2})| - \sqrt{3}|(xz)(\overline{xz})(z^{2})|$$
$$+\sqrt{3}|(yz)(\overline{yz})(z^{2})|)/2\sqrt{3}$$

$$^{2}E_{ga}^{C}$$

$$(t_{2g})^{3} = (|(xy)(xz)(\overline{yz})| - |(xy)(\overline{xz})(yz)|)/\sqrt{2}$$

$$(t_{2g})^{2}(^{1}A_{1g})e_{g} = (|(xy)(\overline{xy})(z^{2})| + |(xz)(\overline{xz})(z^{2})| + |(yz)(\overline{yz})(z^{2})|)/\sqrt{3}$$

$$(t_{2g})^{2}(^{1}E_{g})e_{g} = (-2|(xy)(\overline{xy})(z^{2})| + |(xz)(\overline{xz})(z^{2})| + |(yz)(\overline{yz})(z^{2})|$$
$$-\sqrt{3}|(xz)(\overline{xz})(x^{2}-y^{2})| + \sqrt{3}|(yz)(\overline{yz})(x^{2}-y^{2})|)/2\sqrt{3}$$

$$(e_{g})^{3} = |(z^{2})(x^{2}-y^{2})(\overline{x^{2}-y^{2}})|$$

$$^{2}E_{gb}^{C}$$

$$(t_{2g})^{3} = (-2|(\overline{xy})(xz)(yz)| + |(xy)(\overline{xz})(yz)| + |(xy)(xz)(\overline{yz})|)/\sqrt{6}$$

TABLE 42--Continued

$(t_{2g})^2({}^1A_{1g})e_g \quad = (\,|(xy)(\overline{xy})(x^2-y^2)|+|(xz)(\overline{xz})(x^2-y^2)|$

$\qquad +|(yz)(\overline{yz})(x^2-y^2)|)/\sqrt{3}$

$(t_{2g})^2({}^1E_g)e_g \quad = (2|(xy)(\overline{xy})(x^2-y^2)|-|(xz)(\overline{xz})(x^2-y^2)|$

$\qquad -|(yz)(\overline{yz})(x^2-y^2)|-\sqrt{3}|(xz)(\overline{xz})(z^2)|$

$\qquad +\sqrt{3}|(yz)(\overline{yz})(z^2)|)/2\sqrt{3}$

$(e_g)^3 \quad = |(z^2)(\overline{z^2})(x^2-y^2)|$

${}^2T_{1ga}^C$

$(t_{2g})^3 \quad = (|(xz)(\overline{xz})(xy)|-|(yz)(\overline{yz})(xy)|)/\sqrt{2}$

$(t_{2g})^2({}^3T_{1g})e_g \quad = (-2|(xz)(yz)(\overline{z^2})|+|(xz)(\overline{yz})(z^2)|$

$\qquad +|(\overline{xz})(yz)(z^2)|)/\sqrt{6}$

$(t_{2g})^2({}^1T_{2g})e_g \quad = (|(xz)(\overline{yz})(x^2-y^2)|-|(\overline{xz})(yz)(x^2-y^2)|)/\sqrt{2}$

$t_{2g}(e_g)^2({}^3A_{2g}) \quad = (-2|(\overline{xy})(z^2)(x^2-y^2)|+|(xy)(z^2)(\overline{x^2-y^2})|$

$\qquad +|(xy)(\overline{z^2})(x^2-y^2)|)/\sqrt{6}$

$t_{2g}(e_g)^2({}^1E_g) \quad = (|(xy)(\overline{z^2})(x^2-y^2)|-|(xy)(z^2)(\overline{x^2-y^2})|)/\sqrt{2}$

${}^2T_{1gb}^C$

$(t_{2g})^3 \quad = (|(yz)(\overline{yz})(xz)|-|(xy)(\overline{xy})(xz)|)/\sqrt{2}$

TABLE 42--Continued

$(t_{2g})^2(^3T_{1g})e_g \quad = (2|(yz)(xy)(\overline{z^2})|-|(yz)(xy)(z^2)|-|(\overline{yz})(xy)(z^2)|$

$+2\sqrt{3}|(yz)(xy)(\overline{x^2-y^2})|-\sqrt{3}|(yz)(\overline{xy})(x^2-y^2)|$

$-\sqrt{3}|(\overline{yz})(xy)(x^2-y^2)|)/2\sqrt{6}$

$(t_{2g})^2(^1T_{2g})e_g \quad = (-|(yz)(\overline{xy})(x^2-y^2)|+|(\overline{yz})(xy)(x^2-y^2)|$

$+\sqrt{3}|(yz)(\overline{xy})(z^2)|-\sqrt{3}|(\overline{yz})(xy)(z^2)|)/\sqrt{8}$

$t_{2g}(e_g)^2(^3A_{2g}) \quad = (-2|(\overline{xz})(z^2)(x^2-y^2)|+|(xz)(z^2)(\overline{x^2-y^2})|$

$+|(xz)(\overline{z^2})(x^2-y^2)|)/\sqrt{6}$

$t_{2g}(e_g)^2(^1E_g) \quad = (|(xz)(z^2)(\overline{x^2-y^2})|-|(xz)(\overline{z^2})(x^2-y^2)|$

$+\sqrt{3}|(xz)(z^2)(\overline{z^2})|-\sqrt{3}|(xz)(x^2-y^2)(\overline{x^2-y^2})|)/\sqrt{8}$

$^2T^C_{1gc}$

$(t_{2g})^3 \quad = (|(xy)(\overline{xy})(yz)|-|(xz)(\overline{xz})(yz)|)/\sqrt{2}$

$(t_{2g})^2(^3T_{1g})e_g \quad = (2|(xy)(xz)(\overline{z^2})|-|(xy)(\overline{xz})(z^2)|-|(\overline{xy})(xz)(z^2)|$

$-2\sqrt{3}|(xy)(xz)(\overline{x^2-y^2})|+\sqrt{3}|(xy)(\overline{xz})(x^2-y^2)|$

$+\sqrt{3}|(\overline{xy})(xz)(x^2-y^2)|)/2\sqrt{6}$

$(t_{2g})^2(^1T_{2g})e_g \quad = (-|(xy)(\overline{xz})(x^2-y^2)|+|(\overline{xy})(xz)(x^2-y^2)|$

$+\sqrt{3}|(\overline{xy})(xz)(z^2)|-\sqrt{3}|(xy)(\overline{xz})(z^2)|)/\sqrt{8}$

$t_{2g}(e_g)^2(^3A_{2g}) \quad = (-2|(\overline{yz})(z^2)(x^2-y^2)|+|(yz)(z^2)(\overline{x^2-y^2})|$

$+|(yz)(\overline{z^2})(x^2-y^2)|)/\sqrt{6}$

TABLE 42--Continued

$t_{2g}(e_g)^2(^1E_g) = (|(yz)(z^2)(\overline{x^2-y^2})|-|(yz)(\overline{z^2})(x^2-y^2)|$

$+\sqrt{3}|(yz)(x^2-y^2)(\overline{x^2-y^2})|-\sqrt{3}|(yz)(z^2)(\overline{z^2})|)/\sqrt{8}$

$^2T^C_{2ga}$

$(t_{2g})^3 = (|(xz)(\overline{xz})(xy)|+|(yz)(\overline{yz})(xy)|)/\sqrt{2}$

$(t_{2g})^2(^3T_{1g})e_g = (-2|(xz)(yz)(\overline{x^2-y^2})|+|(xz)(\overline{yz})(x^2-y^2)|$

$+|(\overline{xz})(yz)(x^2-y^2)|)/\sqrt{6}$

$(t_{2g})^2(^1T_{2g})e_g = (|(xz)(\overline{yz})(z^2)|-|(\overline{xz})(yz)(z^2)|)/\sqrt{2}$

$t_{2g}(e_g)^2(^1A_{1g}) = (|(xy)(z^2)(\overline{z^2})|+|(xy)(x^2-y^2)(\overline{x^2-y^2})|)/\sqrt{2}$

$t_{2g}(e_g)^2(^1E_g) = (|(xy)(z^2)(\overline{z^2})|-|(xy)(x^2-y^2)(\overline{x^2-y^2})|)/\sqrt{2}$

$^2T^C_{2gb}$

$(t_{2g})^3 = (|(yz)(\overline{yz})(xz)|+|(xy)(\overline{xy})(xz)|)/\sqrt{2}$

$(t_{2g})^2(^3T_{1g})e_g = (2|(yz)(xy)(\overline{x^2-y^2})|-|(yz)(\overline{xy})(x^2-y^2)|$

$-|(\overline{yz})(xy)(x^2-y^2)|-2\sqrt{3}|(yz)(xy)(\overline{z^2})|$

$+\sqrt{3}|(yz)(\overline{xy})(z^2)|+\sqrt{3}|(\overline{yz})(xy)(z^2)|)/2\sqrt{6}$

$(t_{2g})^2(^1T_{2g})e_g = (-|(yz)(\overline{xy})(z^2)|+|(\overline{yz})(xy)(z^2)|$

$-\sqrt{3}|(yz)(\overline{xy})(x^2-y^2)|+\sqrt{3}|(\overline{yz})(xy)(x^2-y^2)|)/\sqrt{8}$

$t_{2g}(e_g)^2(^1A_{1g}) = (|(xz)(z^2)(\overline{z^2})|+|(xz)(x^2-y^2)(\overline{x^2-y^2})|)/\sqrt{2}$

TABLE 42--Continued

$$\begin{aligned} t_{2g}(e_g)^2({}^1E_g) &= (-|(xz)(z^2)(\overline{z^2})|+|(xz)(x^2-y^2)(\overline{x^2-y^2})| \\ &\quad +\sqrt{3}|(xz)(z^2)(\overline{x^2-y^2})|-\sqrt{3}|(xz)(\overline{z^2})(x^2-y^2)|)/\sqrt{8} \end{aligned}$$

${}^2T^{C}_{2gc}$

$$\begin{aligned} (t_{2g})^3 &= (|(xy)(\overline{xy})(yz)|+|(xz)(\overline{xz})(yz)|)/\sqrt{2} \\ (t_{2g})^2({}^3T_{1g})e_g &= (2|(xy)(xz)(\overline{x^2-y^2})|-|(xy)(\overline{xz})(x^2-y^2)| \\ &\quad -|(xy)(\overline{xz})(x^2-y^2)|+2\sqrt{3}|(xy)(xz)(\overline{z^2})| \\ &\quad -\sqrt{3}|(\overline{xy})(xz)(z^2)|-\sqrt{3}|(\overline{xy})(xz)(z^2)|)/2\sqrt{6} \\ (t_{2g})^2({}^1T_{2g})e_g &= (-|(xy)(\overline{xz})(z^2)|+|(\overline{xy})(xz)(z^2)|+\sqrt{3}|(xy)(\overline{xz})(x^2-y^2)| \\ &\quad -\sqrt{3}|(\overline{xy})(xz)(x^2-y^2)|)/\sqrt{8} \\ t_{2g}(e_g)^2({}^1A_{1g}) &= (|(yz)(z^2(\overline{z^2})|+|(yz)(x^2-y^2)(\overline{x^2-y^2})|)/\sqrt{2} \\ t_{2g}(e_g)^2({}^1E_g) &= (|(yz)(x^2-y^2)(\overline{x^2-y^2})|-|(yz)(z^2)(\overline{z^2})| \\ &\quad -\sqrt{3}|(yz)(z^2)(\overline{x^2-y^2})|+\sqrt{3}|(yz)(\overline{z^2})(x^2-y^2)|)/\sqrt{8} \end{aligned}$$

${}^4A^{C}_{2g}$

$$(t_{2g})^3 = |(xy)(xz)(yz)|$$

${}^4T^{C}_{1ga}$

$$(t_{2g})^2e_g = |(xz)(yz)(z^2)|$$

TABLE 42--Continued

$t_{2g}(e_g)^2$	$= \|(xy)(z^2)(x^2-y^2)\|$
$^4T^C_{1gb}$	
$(t_{2g})^2e_g$	$= (-\|(yz)(xy)(z^2)\|-\sqrt{3}\|(yz)(xy)(x^2-y^2)\|)/2$
$t_{2g}(e_g)^2$	$= \|(xz)(z^2)(x^2-y^2)\|$
$^4T^C_{1gc}$	
$(t_{2g})^2e_g$	$= (-\|(xy)(xz)(z^2)\|+\sqrt{3}\|(xy)(xz)(x^2-y^2)\|)/2$
$t_{2g}(e_g)^2$	$= \|(yz)(z^2)(x^2-y^2)\|$
$^4T^C_{2ga}$	
$(t_{2g})^2e_g$	$= \|(xz)(yz)(x^2-y^2)\|$
$^4T^C_{2gb}$	
$(t_{2g})^2e_g$	$= (-\|(yz)(xy)(x^2-y^2)\|+\sqrt{3}\|(yz)(xy)(z^2)\|)/2$
$^4T^C_{2gc}$	
$(t_{2g})^2e_g$	$= (-\|(xy)(xz)(x^2-y^2)\|-\sqrt{3}\|(xy)(xz)(z^2)\|)/2$

[k] J. R. Perumareddi, Coord. Chem. Rev., 4, 73(1969).

$$^2E_{ga}[(e_g)^3] = |(z^2)(x^2-y^2)(\overline{x^2-y^2})| \text{ and}$$

$$^2E_{ga}[(e_g)^3] = (0)[(2)+(-2)][(\bar{2})+(-\bar{2})]/2$$

and finally,

$$^2E_{ga}[(e_g)^3] = [(2\bar{2}0)-(20-\bar{2})+(\bar{2}0-2)+(0-2-\bar{2})]/2.$$

Alternately, the interelectronic repulsion energies for the strong field case can be calculated using the J(ab) and K(ab) integrals for the real forms of the d orbitals. These integrals have been tabulated by Ballhausen.[1]

The complete strong field energy matrices for the cubic case of d^3, without inclusion of the spin-orbit interaction, are given in Table 43.

The Spin Orbit Interaction

The space and spin combinations which will form the spin-adapted wave functions for the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme are identical to those of the $\{L, S, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme. These are given in Table 34.

The doublet and quartet spin-adapted wave functions in microstate form are then derived as was done in the weak field coupling scheme. Only here use is made of the cubic strong field wave functions, (cf. Table 42), for the orbital half of each wave function.

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[1] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., New York, 1962.

TABLE 43

The Elements of the Cubic Energy Matrices (the H'_{jk}'s), Spin-Orbit Interaction Neglected, for d^3 Electronic Configuration in the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ Coupling Scheme

	$^2A^C_{1g}$	
j	k	H'_{jk}
$(t_{2g})^2e_g$	$(t_{2g})^2e_g$	-11B+3C-2Dq
	$^2A^C_{2g}$	
$(t_{2g})^2e_g$	$(t_{2g})^2e_g$	9B+3C-2Dq
	$^2E^C_g$	
$(t_{2g})^3$	$(t_{2g})^3$	-6B+3C-12Dq
$(t_{2g})^3$	$(t_{2g})^2(^1A_{1g})e_g$	$-6\sqrt{2}B$
$(t_{2g})^3$	$(t_{2g})^2(^1E_g)e_g$	$-3\sqrt{2}B$
$(t_{2g})^3$	$(e_g)^3$	0
$(t_{2g})^2(^1A_{1g})e_g$	$(t_{2g})^2(^1A_{1g})e_g$	8B+6C-2Dq
$(t_{2g})^2(^1A_{1g})e_g$	$(t_{2g})^2(^1E_g)e_g$	10B
$(t_{2g})^2(^1A_{1g})e_g$	$(e_g)^3$	$\sqrt{3}(2B+C)$
$(t_{2g})^2(^1E_g)e_g$	$(t_{2g})^2(^1E_g)e_g$	-B+3C-2Dq
$(t_{2g})^2(^1E_g)e_g$	$(e_g)^3$	$2\sqrt{3}B$
$(e_g)^3$	$(e_g)^3$	-8B+4C+18Dq

TABLE 43--Continued

	$^2T_{1g}^C$	
j	k	H'_{jk}
$(t_{2g})^3$	$(t_{2g})^3$	-6B+3C-12Dq
$(t_{2g})^3$	$(t_{2g})^2(^3T_{1g})e_g$	3B
$(t_{2g})^3$	$(t_{2g})^2(^1T_{2g})e_g$	-3B
$(t_{2g})^3$	$t_{2g}(e_g)^2(^3A_{2g})$	0
$(t_{2g})^3$	$t_{2g}(e_g)^2(^1E_g)$	$-2\sqrt{3}B$
$(t_{2g})^2(^3T_{1g})e_g$	$(t_{2g})^2(^3T_{1g})e_g$	3C-2Dq
$(t_{2g})^2(^3T_{1g})e_g$	$(t_{2g})^2(^1T_{2g})e_g$	-3B
$(t_{2g})^2(^3T_{1g})e_g$	$t_{2g}(e_g)^2(^3A_{2g})$	-3B
$(t_{2g})^2(^3T_{1g})e_g$	$t_{2g}(e_g)^2(^1Eg)$	$-3\sqrt{3}B$
$(t_{2g})^2(^1T_{2g})e_g$	$(t_{2g})^2(^1T_{2g})e_g$	-6B+3C-2Dq
$(t_{2g})^2(^1T_{2g})e_g$	$t_{2g}(e_g)^2(^3A_{2g})$	3B
$(t_{2g})^2(^1T_{2g})e_g$	$t_{2g}(e_g)^2(^1E_g)$	$\sqrt{3}B$
$t_{2g}(e_g)^2(^3A_{2g})$	$t_{2g}(e_g)^2(^3A_{2g})$	-6B+3C+8Dq
$t_{2g}(e_g)^2(^3A_{2g})$	$t_{2g}(e_g)^2(^1E_g)$	$2\sqrt{3}B$
$t_{2g}(e_g)^2(^1E_g)$	$t_{2g}(e_g)^2(^1E_g)$	-2B+3C+8Dq

TABLE 43--Continued

	${}^2T^C_{2g}$	
j	k	H'_{jk}
$(t_{2g})^3$	$(t_{2g})^3$	5C-12Dq
$(t_{2g})^3$	$(t_{2g})^2(^3T_{1g})e_g$	$3\sqrt{3}B$
$(t_{2g})^3$	$(t_{2g})^2(^1T_{2g})e_g$	$-5\sqrt{3}B$
$(t_{2g})^3$	$t_{2g}(e_g)^2(^1A_{1g})$	4B+2C
$(t_{2g})^3$	$t_{2g}(e_g)^2(^1E_g)$	-2B
$(t_{2g})^2(^3T_{1g})e_g$	$(t_{2g})^2(^3T_{1g})e_g$	-6B+3C-2Dq
$(t_{2g})^2(^3T_{1g})e_g$	$(t_{2g})^2(^1T_{2g})3_g$	-3B
$(t_{2g})^2(^3T_{1g})e_g$	$t_{2g}(e_g)^2(^1A_{1g})$	$3\sqrt{3}B$
$(t_{2g})^2(^3T_{1g})e_g$	$t_{2g}(e_g)^2(^1E_g)$	$-3\sqrt{3}B$
$(t_{2g})^2(^1T_{2g})e_g$	$(t_{2g})^2(^1T_{2g})e_g$	4B+3C-2Dq
$(t_{2g})^2(^1T_{2g})e_g$	$t_{2g}(e_g)^2(^1A_{1g})$	$-\sqrt{3}B$
$(t_{2g})^2(^1T_{2g})e_g$	$t_{2g}(e_g)^2(^1E_g)$	$-\sqrt{3}B$
$t_{2g}(e_g)^2(^1A_{1g})$	$t_{2g}(e_g)^2(^1A_{1g})$	6B+5C+8Dq
$t_{2g}(e_g)^2(^1A_{1g})$	$t_{2g}(e_g)^2(^1E_g)$	-10B
$t_{2g}(e_g)^2(^1E_g)$	$t_{2g}(e_g)^2(^1E_g)$	-2B+3C+8Dq

TABLE 43--Continued

	$^4A_{2g}^C$	
j	k	H'_{jk}
$(t_{2g})^3$	$(t_{2g})^3$	$-15B-12Dq$
	$^4T_{1g}^C$	
$(t_{2g})^2e_g$	$(t_{2g})^2e_g$	$-3B-2Dq$
$(t_{2g})^2e_g$	$t_{2g}(e_g)^2$	$6B$
$t_{2g}(e_g)^2$	$t_{2g}(e_g)^2$	$-12B+8Dq$
	$^4T_{2g}^C$	
$(t_{2g})^2e_g$	$(t_{2g})^2e_g$	$-15B+2Dq$

Note, however, that when connecting a doublet Γ_{6b}^{S} spin function, (M_s = -1/2), to an orbital function from Table 42 which has initially M_s = +1/2 (in either all or part of the wave function), then we must change the sign of that part of the strong field orbital wave function which had initially M_s = +1/2. This must be done to maintain a phase consistency within the transformation properties of the spin.

These strong field spin-adapted wave functions in microstate form are given in Table 44 for the components of $\Gamma_6{}^C$ and $\Gamma_7{}^C$ and for the a and c components of $\Gamma_8{}^C$.

The spin-orbit perturbation in the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme block diagonalizes the secular determinant into two 9 by 9's ($\Gamma_6{}^C$ and $\Gamma_7{}^C$) and one 21 by 21 ($\Gamma_8{}^C$). This is consistent, as it must be, with the $\{L, S, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme, (cf. Fig. 9).

To calculate the matrix elements (the H'_{jk}'s) for the spin-orbit perturbation we can readily convert the spin-adapted wave functions of Table 44 from strong field microstate form to weak field microstate form using the relations (94a-e). Once this is accomplished we can calculate the matrix elements, as multiples of the spin-orbit parameter zeta (ζ), exactly as was done in the two weak field coupling schemes.

The resulting non-zero matrix elements for the spin-orbit perturbation of the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme are given in Table 45.

TABLE 44

The Spin-Adapted Wave Functions in Microstate Form for the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ Coupling Scheme

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The numbering of the eigenvectors used below is the same as that given in Table 45a. Only the a components of Γ_6^C and Γ_7^C and only the a and c components of Γ_8^C are given.

Γ_{6a}^C

$$\begin{aligned}(1) = {} & (-2|(xy)(\overline{xy})(z^2)|+|(yz)(\overline{yz})(z^2)|+|(xz)(\overline{xz})(z^2)| \\ & +\sqrt{3}|(xz)(\overline{xz})(x^2-y^2)|-\sqrt{3}|(yz)(\overline{yz})(x^2-y^2)|)/2\sqrt{3}\end{aligned}$$

$$\begin{aligned}(2) = {} & (-|(xz)(\overline{xz})(xy)|+|(yz)(\overline{yz})(xy)|-i|(yz)(\overline{yz})(\overline{xz})| \\ & +i|(xy)(\overline{xy})(\overline{xz})|-|(xy)(\overline{xy})(\overline{yz})|+|(xz)(\overline{xz})(\overline{yz})|)/\sqrt{6}\end{aligned}$$

$$\begin{aligned}(3) = {} & (4|(xz)(yz)(\overline{z^2})|-2|(xz)(\overline{yz})(z^2)|-2|(\overline{xz})(yz)(z^2)| \\ & +2i|(\overline{yz})(\overline{xy})(z^2)|-i|(\overline{yz})(xy)(\overline{z^2})|-i|(yz)(x\bar{y})(\overline{z^2})| \\ & +2i\sqrt{3}|(\overline{yz})(\overline{xy})(x^2-y^2)|-i\sqrt{3}|(\overline{yz})(xy)(\overline{x^2-y^2})|-i\sqrt{3}|(yz)(\overline{xy})(\overline{x^2-y^2})| \\ & +2|(\overline{xy})(\overline{xz})(z^2)|-|(\overline{xy})(xz)(\overline{z^2})|-|(xy)(\overline{xz})(\overline{z^2})| \\ & -2\sqrt{3}\ (\overline{xy})(\overline{xz})(x^2-y^2)|+\sqrt{3}|(\overline{xy})(xz)(\overline{x^2-y^2})|+\sqrt{3}|(xy)(\overline{xz})(\overline{x^2-y^2})|)/6\sqrt{2}\end{aligned}$$

$$\begin{aligned}(4) = {} & (-2|(xz)(\overline{yz})(x^2-y^2)|+2|(\overline{xz})(yz)(x^2-y^2)|-i|(\overline{yz})(xy)(\overline{x^2-y^2})| \\ & +i|(yz)(\overline{xy})(\overline{x^2-y^2})|+i\sqrt{3}|(\overline{yz})(xy)(\overline{z^2})|-i\sqrt{3}|(yz)(\overline{xy})(\overline{z^2})| \\ & -|(\overline{xy})(xz)(\overline{x^2-y^2})|+|(xy)(\overline{xz})(\overline{x^2-y^2})|+\sqrt{3}|(xy)(\overline{xz})(\overline{z^2})| \\ & -\sqrt{3}|(\overline{xy})(xz)(\overline{z^2})|)/2\sqrt{6}\end{aligned}$$

$$\begin{aligned}(5) = {} & (2|(\overline{xy})(z^2)(x^2-y^2)|-|(xy)(z^2)(\overline{x^2-y^2})|-|(xy)(\overline{z^2})(x^2-y^2)| \\ & -2i|(xz)(\overline{z^2})(\overline{x^2-y^2})|+i|(\overline{xz})(\overline{z^2})(x^2-y^2)|+i|(\overline{xz})(z^2)(\overline{x^2-y^2})| \\ & -2|(yz)(\overline{z^2})(\overline{x^2-y^2})|+|(\overline{yz})(\overline{z^2})(x^2-y^2)|+|(\overline{yz})(z^2)(\overline{x^2-y^2})|)/3\sqrt{2}\end{aligned}$$

TABLE 44--Continued

$(6) = (2|(xy)(z^2)(x^2\overline{-}y^2)|-2|(xy)(\overline{z}^2)(x^2-y^2)|+i|(\overline{x}z)(\overline{z}^2)(x^2-y^2)|$
$-i|(\overline{x}z)(z^2)(x^2\overline{-}y^2)|-i\sqrt{3}|(\overline{x}z)(z^2)(\overline{z}^2)|+i\sqrt{3}|(\overline{x}z)(x^2-y^2)(x^2\overline{-}y^2)|$
$+|(yz)(\overline{z}^2)(x^2-y^2)|-|(\overline{y}z)(z^2)(x^2\overline{-}y^2)|-\sqrt{3}|(\overline{y}z)(x^2-y^2)(x^2\overline{-}y^2)|$
$+\sqrt{3}|(\overline{y}z)(z^2)(\overline{z}^2)|)/2\sqrt{6}$

$(7) = (-4i|(xz)(yz)(\overline{z}^2)|-4i|(xz)(\overline{y}z)(z^2)|-4i|(\overline{x}z)(yz)(z^2)|$
$-|(yz)(\overline{x}y)(\overline{z}^2)|-|(\overline{y}z)(\overline{x}y)(z^2)|-|(\overline{y}z)(xy)(\overline{z}^2)|$
$-\sqrt{3}|(yz)(\overline{x}y)(x^2\overline{-}y^2)|-\sqrt{3}|(\overline{y}z)(\overline{x}y)(x^2-y^2)|-\sqrt{3}|(\overline{y}z)(xy)(x^2\overline{-}y^2)|$
$-3|(yz)(xy)(z^2)|-3\sqrt{3}|(yz)(xy)(x^2-y^2)|+i|(xy)(\overline{x}z)(\overline{z}^2)|$
$+i|(\overline{x}y)(xz)(\overline{z}^2)|+i|(\overline{x}y)(\overline{x}z)(z^2)|-i\sqrt{3}|(xy)(\overline{x}z)(x^2\overline{-}y^2)|$
$-i\sqrt{3}|(\overline{x}y)(xz)(x^2\overline{-}y^2)|-i\sqrt{3}|(\overline{x}y)(\overline{x}z)(x^2-y^2)|-3i|(xy)(xz)(z^2)|$
$+3i\sqrt{3}|(xy)(xz)(x^2-y^2)|)/12$

$(8) = (-2i|(xy)(z^2)(x^2\overline{-}y^2)|-2i|(xy)(\overline{z}^2)(x^2-y^2)|$
$-2i|(\overline{x}y)(z^2)(x^2-y^2)|+|(xz)(\overline{z}^2)(x^2\overline{-}y^2)|+|(\overline{x}z)(z^2)(x^2\overline{-}y^2)|$
$+|(\overline{x}z)(\overline{z}^2)(x^2-y^2)|+3|(xz)(z^2)(x^2-y^2)|-i|(yz)(\overline{z}^2)(x^2\overline{-}y^2)|$
$-i|(\overline{y}z)(z^2)(x^2\overline{-}y^2)|-i|(\overline{y}z)(\overline{z}^2)(x^2-y^2)|+3i|(yz)(z^2)(x^2-y^2)|)/6$

$(9) = (4|(\overline{x}z)(\overline{y}z)(x^2\overline{-}y^2)|-i|(yz)(xy)(x^2-y^2)|+i\sqrt{3}|(yz)(xy)(z^2)|$
$-|(xy)(xz)(x^2-y^2)|-\sqrt{3}|(xy)(xz)(z^2)|+i|(yz)(x\overline{y})(x^2\overline{-}y^2)|$
$+i|(\overline{y}z)(xy)(x^2\overline{-}y^2)|+i|(\overline{y}z)(\overline{x}y)(x^2-y^2)|-i\sqrt{3}|(yz)(\overline{x}y)(\overline{z}^2)|$
$-i\sqrt{3}|(\overline{y}z)(xy)(\overline{z}^2)|-i\sqrt{3}|(\overline{y}z)(\overline{x}y)(z^2)|-|(xy)(\overline{x}z)(x^2\overline{-}y^2)|$
$-|(\overline{x}y)(xz)(x^2\overline{-}y^2)|-|(\overline{x}y)(\overline{x}z)(x^2-y^2)|-\sqrt{3}|(xy)(\overline{x}z)(\overline{z}^2)|$
$-\sqrt{3}|(\overline{x}y)(xz)(\overline{z}^2)|-\sqrt{3}|(\overline{x}y)(\overline{x}z)(z^2)|)/4\sqrt{3}$

TABLE 44--Continued

Γ^{C}_{7a}

$$\begin{aligned}(1) = {} & (-2|(xy)(\bar{x}y)(x^2\overline{-}y^2)|+|(xz)(\bar{x}z)(x^2\overline{-}y^2)|+|(yz)(\bar{y}z)(x^2\overline{-}y^2)|\\ & -\sqrt{3}|(xz)(\bar{x}z)(\bar{z}^2)|+\sqrt{3}|(yz)(\bar{y}z)(\bar{z}^2)|)/2\sqrt{3}\end{aligned}$$

$$\begin{aligned}(2) = {} & (i|(xz)(\bar{x}z)(\bar{x}y)|+i|(yz)(\bar{y}z)(\bar{x}y)|-|(yz)(y\bar{z})(xz)|\\ & -|(xy)(\bar{x}y)(xz)|-i|(xy)(\bar{x}y)(yz)|-i|(xz)(\bar{x}z)(yz)|)/\sqrt{6}\end{aligned}$$

$$\begin{aligned}(3) = {} & (4i|(\bar{x}z)(\bar{y}z)(x^2-y^2)|-2i|(\bar{x}z)(yz)(x^2\overline{-}y^2)|\\ & -2i|(xz)(\bar{y}z)(x^2\overline{-}y^2)|-2|(yz)(xy)(x^2\overline{-}y^2)|+|(yz)(\bar{x}y)(x^2-y^2)\\ & +|(\bar{y}z)(xy)(x^2-y^2)|+2\sqrt{3}|(yz)(xy)(\bar{z}^2)|-\sqrt{3}|(yz)(\bar{x}y)(z^2)|\\ & -\sqrt{3}|(\bar{y}z)(xy)(z^2)|-2i|(xy)(xz)(x^2\overline{-}y^2)|+i|(xy)(\bar{x}z)(x^2-y^2)|\\ & +i|(\bar{x}y)(xz)(x^2-y^2)|-2i\sqrt{3}|(xy)(xz)(\bar{z}^2)|+i\sqrt{3}|(xy)(\bar{x}z)(z^2)|\\ & +i\sqrt{3}|(\bar{x}y)(xz)(z^2)|)/6\sqrt{2}\end{aligned}$$

$$\begin{aligned}(4) = {} & (-2i|(\bar{x}z)(yz)(\bar{z}^2)|+2i|(xz)(\bar{y}z)(\bar{z}^2)|+|(yz)(\bar{x}y)(z^2)|\\ & -|(y\bar{z})(xy)(z^2)|+\sqrt{3}|(yz)(\bar{x}y)(x^2-y^2)|-\sqrt{3}|(y\bar{z})(xy)(x^2-y^2)|\\ & +i|(xy)(\bar{x}z)(z^2)|-i|(\bar{x}y)(xz)(z^2)|-i\sqrt{3}|(xy)(\bar{x}z)(x^2-y^2)|\\ & +i\sqrt{3}|(\bar{x}y)(xz)(x^2-y^2)|)/2\sqrt{6}\end{aligned}$$

$$\begin{aligned}(5) = {} & (i|(\bar{x}y)(z^2)(\bar{z}^2)|+i|(\bar{x}y)(x^2-y^2)(x^2\overline{-}y^2)|-|(xz)(z^2)(\bar{z}^2)|\\ & -|(xz)(x^2-y^2)(x^2\overline{-}y^2)|-i|(yz)(z^2)(\bar{z}^2)|-i|(yz)(x^2-y^2)(x^2\overline{-}y^2)|)/\sqrt{6}\end{aligned}$$

$$\begin{aligned}(6) = {} & (2i|(\bar{x}y)(z^2)(\bar{z}^2)|-2i|(\bar{x}y)(x^2-y^2)(x^2\overline{-}y^2)|+|(xz)(z^2)(\bar{z}^2)|\\ & -|(xz)(x^2-y^2)(x^2\overline{-}y^2)|-\sqrt{3}|(xz)(z^2)(x^2\overline{-}y^2)|+\sqrt{3}|(xz)(\bar{z}^2)(x^2-y^2)|\\ & -i|(yz)(x^2-y^2)(x^2\overline{-}y^2)|+i|(yz)(z^2)(\bar{z}^2)|+i\sqrt{3}|(yz)(z^2)(x^2\overline{-}y^2)|\\ & -i\sqrt{3}|(yz)(\bar{z}^2)(x^2-y^2)|)/2\sqrt{6}\end{aligned}$$

TABLE 44--Continued

$(7) = (4i|(xz)(yz)(z^2)|+|(\bar{y}z)(x\bar{y})(\bar{z}^2)|+\sqrt{3}|(\bar{y}z)(\bar{x}y)(x^2\bar{-}y^2)|$
$+i|(\bar{x}y)(\bar{x}z)(\bar{z}^2)|-i\sqrt{3}|(\bar{x}y)(\bar{x}z)(x^2\bar{-}y^2)|-|(yz)(xy)(\bar{z}^2)|$
$-|(yz)(\bar{x}y)(z^2)|-|(\bar{y}z)(xy)(z^2)|-\sqrt{3}|(yz)(xy)(x^2\bar{-}y^2)|$
$-\sqrt{3}|(yz)(\bar{x}y)(x^2-y^2)|-\sqrt{3}|(\bar{y}z)(xy)(x^2-y^2)|+i|(xy)(xz)(\bar{z}^2)|$
$+i|(xy)(\bar{x}z)(z^2)|+i|(\bar{x}y)(xz)(z^2)|-i\sqrt{3}|(xy)(xz)(x^2\bar{-}y^2)|$
$-i\sqrt{3}|(xy)(\bar{x}z)(x^2-y^2)|-i\sqrt{3}|(\bar{x}y)(xz)(x^2-y^2)|)/4\sqrt{3}$

$(8) = (2i|(xy)(z^2)(x^2-y^2)|-|(\bar{x}z)(\bar{z}^2)(x^2\bar{-}y^2)|-i|(\bar{y}z)(\bar{z}^2)(x^2\bar{-}y^2)|$
$+|(xz)(z^2)(x^2\bar{-}y^2)|+|(xz)(\bar{z}^2)(x^2-y^2)|+|(\bar{x}z)(z^2)(x^2-y^2)|$
$-i|(yz)(z^2)(x^2\bar{-}y^2)|-i|(yz)(\bar{z}^2)(x^2-y^2)|-i|(\bar{y}z)(z^2)(x^2-y^2)|)/2\sqrt{3}$

$(9) = (-4|(xz)(\bar{y}z)(x^2\bar{-}y^2)|-4|(\bar{x}z)(yz)(x^2\bar{-}y^2)|$
$-4|(\bar{x}z)(\bar{y}z)(x^2-y^2)|+i|(yz)(xy)(x^2\bar{-}y^2)|+i|(yz)(\bar{x}y)(x^2-y^2)|$
$+i|(\bar{y}z)(xy)(x^2-y^2)|-i\sqrt{3}|(yz)(xy)(\bar{z}^2)|-i\sqrt{3}|(yz)(\bar{x}y)(z^2)|$
$-i\sqrt{3}|(\bar{y}z)(xy)(z^2)|-|(xy)(xz)(x^2\bar{-}y^2)|-|(xy)(\bar{x}z)(x^2-y^2)|$
$-|(x\bar{y})(xz)(x^2-y^2)|-\sqrt{3}|(xy)(xz)(\bar{z}^2)|-\sqrt{3}|(xy)(\bar{x}z)(z^2)|$
$-\sqrt{3}|(\bar{x}y)(xz)(z^2)| + 3i|(\bar{y}z)(\bar{x}y)(x^2\bar{-}y^2)|-3i\sqrt{3}|(\bar{y}z)(\bar{x}y)(\bar{z}^2)|$
$+3|(\bar{x}y)(\bar{x}z)(x^2\bar{-}y^2)|+3\sqrt{3}|(x\bar{y})(\bar{x}z)(\bar{z}^2)|)/12$

Γ_{8a}^{C}

$(1) = (|(xy)(\bar{x}z)(yz)|-|(xy)(xz)(\bar{y}z)|)/\sqrt{2}$

$(2) = (-|(xy)(\bar{x}y)(z^2)|-|(xz)(\bar{x}z)(z^2)|-|(yz)(\bar{y}z)(z^2)|)/\sqrt{3}$

TABLE 44--Continued

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(3) $= (2|(xy)(\bar{x}y)(z^{2})|-|(xz)(\bar{x}z)(z^{2})|-|(yz)(\bar{y}z)(z^{2})|$

$+\sqrt{3}|(xz)(\bar{x}z)(x^{2}-y^{2})|-\sqrt{3}|(yz)(\bar{y}z)(x^{2}-y^{2})|)/2\sqrt{3}$

(4) $= -|(z^{2})(x^{2}-y^{2})(x^{2}\bar{-}y^{2})|$

(5) $= (-2|(xz)(\bar{x}z)(xy)|+2|(yz)(\bar{y}z)(xy)|+i|(yz)(\bar{y}z)(\bar{x}z)|$

$-i|(xy)(\bar{x}y)(\bar{x}z)|+|(xy)(\bar{x}y)(\bar{y}z)|-|(xz)(\bar{x}z)(\bar{y}z)|)/2\sqrt{3}$

(6) $= (8|(xz)(yz)(\bar{z}^{2})|-4|(xz)(\bar{y}z)(z^{2})|-4|(\bar{x}z)(yz)(z^{2})|$

$-2i|(\bar{y}z)(\bar{x}y)(z^{2})|+i|(\bar{y}z)(xy)(\bar{z}^{2})|+i|(yz)(\bar{x}y)(\bar{z}^{2})|$

$-2i\sqrt{3}|(\bar{y}z)(\bar{x}y)(x^{2}-y^{2})|+i\sqrt{3}|(\bar{y}z)(xy)(x^{2}\bar{-}y^{2})|$

$+i\sqrt{3}|(yz)(x\bar{y})(x^{2}\bar{-}y^{2})|-2|(\bar{x}y)(\bar{x}z)(z^{2})|+|(\bar{x}y)(xz)(\bar{z}^{2})|$

$+|(xy)(\bar{x}z)(\bar{z}^{2})|+2\sqrt{3}|(\bar{x}y)(\bar{x}z)(x^{2}-y^{2})|-\sqrt{3}|(\bar{x}y)(xz)(x^{2}\bar{-}y^{2})|$

$-\sqrt{3}|(xy)(\bar{x}z)(x^{2}\bar{-}y^{2})|)/12$

(7) $= (-4|(xz)(\bar{y}z)(x^{2}-y^{2})|+4|(\bar{x}z)(yz)(x^{2}-y^{2})|$

$+i|(\bar{y}z)(xy)(x^{2}\bar{-}y^{2})|-i|(yz)(\bar{x}y)(x^{2}\bar{-}y^{2})|-i\sqrt{3}|(\bar{y}z)(xy)(\bar{z}^{2})|$

$+i\sqrt{3}|(yz)(\bar{x}y)(\bar{z}^{2})|+|(\bar{x}y)(xz)(x^{2}\bar{-}y^{2})|-|(xy)(\bar{x}z)(x^{2}\bar{-}y^{2})|$

$-\sqrt{3}|(xy)(\bar{x}z)(\bar{z}^{2})|+\sqrt{3}|(\bar{x}y)(xz)(\bar{z}^{2})|)/4\sqrt{3}$

(8) $= (4|(\bar{x}y)(z^{2})(x^{2}-y^{2})|-2|(xy)(z^{2})(x^{2}\bar{-}y^{2})|-2|(xy)(\bar{z}^{2})(x^{2}-y^{2})|$

$+2i|(xz)(\bar{z}^{2})(x^{2}-y^{2})|-i|(\bar{x}z)(\bar{z}^{2})(x^{2}-y^{2})|-i|(\bar{x}z)(z^{2})(x^{2}\bar{-}y^{2})|$

$+2|(yz)(\bar{z}^{2})(x^{2}\bar{-}y^{2})|-|(\bar{y}z)(\bar{z}^{2})(x^{2}-y^{2})|-|(\bar{y}z)(z^{2})(x^{2}\bar{-}y^{2})|)/6$

TABLE 44--Continued

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(9) $= (4|(xy)(z^{2})(x^{2}\overline{-}y^{2})|-4|(xy)(\overline{z}^{2})(x^{2}-y^{2})|-i|(\overline{x}z)(\overline{z}^{2})(x^{2}-y^{2})|$

$+i|(\overline{x}z)(z^{2})(x^{2}\overline{-}y^{2})|+i\sqrt{3}|(\overline{x}z)(z^{2})(\overline{z}^{2})|-i\sqrt{3}|(\overline{x}z)(x^{2}-y^{2})(x^{2}\overline{-}y^{2})|$

$-|(\overline{y}z)(\overline{z}^{2})(x^{2}-y^{2})|+|(\overline{y}z)(z^{2})(x^{2}\overline{-}y^{2})|+\sqrt{3}|(\overline{y}z)(x^{2}-y^{2})(x^{2}\overline{-}y^{2})|$

$-\sqrt{3}|(\overline{y}z)(z^{2})(\overline{z}^{2})|)/4\sqrt{3}$

(10) $= (-|(yz)(\overline{y}z)(\overline{x}z)|-|(xy)(\overline{x}y)(\overline{x}z)|-i|(xy)(\overline{x}y)(\overline{y}z)|$

$-i|(xz)(\overline{x}z)(\overline{y}z)|)/2$

(11) $= (2|(\overline{y}z)(\overline{x}y)(x^{2}-y^{2})|-|(\overline{y}z)(xy)(x^{2}\overline{-}y^{2})|-|(yz)(\overline{x}y)(x^{2}\overline{-}y^{2})|$

$-2\sqrt{3}|(\overline{y}z)(\overline{x}y)(z^{2})|+\sqrt{3}|(\overline{y}z)(xy)(\overline{z}^{2})|+\sqrt{3}|(yz)(\overline{x}y)(\overline{z}^{2})|$

$+2i|(\overline{x}y)(\overline{x}z)(x^{2}-y^{2})|-i|(\overline{x}y)(xz)(x^{2}\overline{-}y^{2})|-i|(xy)(\overline{x}z)(x^{2}\overline{-}y^{2})|$

$+2i\sqrt{3}|(\overline{x}y)(\overline{x}z)(z^{2})|-i\sqrt{3}|(\overline{x}y)(xz)(\overline{z}^{2})|-i\sqrt{3}|(xy)(\overline{x}z)(\overline{z}^{2})|)/4\sqrt{3}$

(12) $= (-|(\overline{y}z)(xy)(\overline{z}^{2})|+|(yz)(\overline{x}y)(\overline{z}^{2})|-\sqrt{3}|(\overline{y}z)(xy)(x^{2}\overline{-}y^{2})|$

$+\sqrt{3}|(yz)(\overline{x}y)(x^{2}\overline{-}y^{2})|-i|(\overline{x}y)(xz)(\overline{z}^{2})|+i|(xy)(\overline{x}z)(\overline{z}^{2})|$

$+i\sqrt{3}|(\overline{x}y)(xz)(x^{2}\overline{-}y^{2})|-i\sqrt{3}|(xy)(\overline{x}z)(x^{2}\overline{-}y^{2})|)/4$

(13) $= (-|(\overline{x}z)(z^{2})(\overline{z}^{2})|-|(\overline{x}z)(x^{2}-y^{2})(x^{2}\overline{-}y^{2})|$

$-i|(\overline{y}z)(z^{2})(\overline{z}^{2})|-i|(\overline{y}z)(x^{2}-y^{2})(x^{2}\overline{-}y^{2})|)/2$

(14) $= (|(\overline{x}z)(z^{2})(\overline{z}^{2})|-|(\overline{x}z)(x^{2}-y^{2})(x^{2}\overline{-}y^{2})|+\sqrt{3}|(\overline{x}z)(\overline{z}^{2})(x^{2}-y^{2})|$

$-\sqrt{3}|(x\overline{z})(z^{2})(x^{2}\overline{-}y^{2})|-i|(\overline{y}z)(x^{2}-y^{2})(x^{2}\overline{-}y^{2})|+i|(\overline{y}z)(z^{2})(\overline{z}^{2})|$

$-i\sqrt{3}|(\overline{y}z)(\overline{z}^{2})(x^{2}-y^{2})|+i\sqrt{3}|(\overline{y}z)(z^{2})(x^{2}\overline{-}y^{2})|)/4$

(15) $= |(\overline{x}y)(\overline{x}z)(\overline{y}z)|$

TABLE 44--Continued

$(16) = (2i|(xz)(yz)(\overline{z^2})|+2i|(xz)(\bar{y}z)(z^2)|+2i|(\bar{x}z)(yz)(z^2)|$
$-|(\bar{y}z)(\bar{x}y)(z^2)|-|(\bar{y}z)(xy)(\overline{z^2})|-|(yz)(\bar{x}y)(\overline{z^2})|$
$-\sqrt{3}|(\bar{y}z)(\bar{x}y)(x^2-y^2)|-\sqrt{3}|(\bar{y}z)(xy)(\overline{x^2-y^2})|-\sqrt{3}|(yz)(\bar{x}y)(\overline{x^2-y^2})|$
$+i|(\bar{x}y)(\bar{x}z)(z^2)|+i|(x\bar{y})(xz)(\overline{z^2})|+i|(xy)(\bar{x}z)(\overline{z^2})|$
$-i\sqrt{3}|(\bar{x}y)(\bar{x}z)(x^2-y^2)|-i\sqrt{3}|(x\bar{y})(xz)(\overline{x^2-y^2})|-i\sqrt{3}|(xy)(\bar{x}z)(\overline{x^2-y^2})|)/6$

$(17) = (4i|(xy)(yz)(\overline{z^2})|+4i|(xz)(\bar{y}z)(z^2)|+4i|(\bar{x}z)(yz)(z^2)|$
$+|(yz)(\bar{x}y)(\overline{z^2})|+|(\bar{y}z)(xy)(\overline{z^2})|+|(\bar{y}z)(\bar{x}y)(z^2)|$
$+\sqrt{3}|(yz)(\bar{x}y)(\overline{x^2-y^2})|+\sqrt{3}|(\bar{y}z)(xy)(\overline{x^2-y^2})|+\sqrt{3}|(\bar{y}z)(\bar{x}y)(x^2-y^2)|$
$-i|(xy)(\bar{x}z)(\overline{z^2})|-i|(\bar{x}y)(xz)(\overline{z^2})|-i|(\bar{x}y)(\bar{x}z)(z^2)|$
$-3|(yz)(xy)(z^2)|+3\sqrt{3}|(xy)(yz)(x^2-y^2)|-3i|(xy)(xz)(z^2)|$
$+3i\sqrt{3}|(xy)(xz)(x^2-y^2)|+i\sqrt{3}|(xy)(\bar{x}z)(\overline{x^2-y^2})|$
$+i\sqrt{3}|(\bar{x}y)(xz)(\overline{x^2-y^2})|+i\sqrt{3}|(\bar{x}y)(\bar{x}z)(x^2-y^2)|)/12$

$(18) = (i|(xy)(z^2)(\overline{x^2-y^2})|+i|(xy)(\overline{z^2})(x^2-y^2)|+i|(\bar{x}y)(z^2)(x^2-y^2)|$
$+|(xz)(\overline{z^2})(\overline{x^2-y^2})|+|(\bar{x}z)(z^2)(\overline{x^2-y^2})|+|(\bar{x}z)(\overline{z^2})(x^2-y^2)|$
$-i|(\bar{y}z)(\overline{z^2})(x^2-y^2)|-i|(\bar{y}z)(z^2)(\overline{x^2-y^2})|-i|(yz)(\overline{z^2})(\overline{x^2-y^2})|)/3$

$(19) = (2i|(xy)(z^2)(\overline{x^2-y^2})|+2i|(xy)(\overline{z^2})(x^2-y^2)|+2i|(\bar{x}y)(z^2)(x^2-y^2)|$
$-|(xz)(\overline{z^2})(\overline{x^2-y^2})|-|(\bar{x}z)(z^2)(\overline{x^2-y^2})|-|(\bar{x}z)(\overline{z^2})(x^2-y^2)|$
$+i|(\bar{y}z)(\overline{z^2})(x^2-y^2)|+i|(\bar{y}z)(z^2)(\overline{x^2-y^2})|+i|(yz)(\overline{z^2})(\overline{x^2-y^2})|$
$+3|(xz)(z^2)(x^2-y^2)|+3i|(yz)(z^2)(x^2-y^2)|)/6$

$(20) = (-2|(\bar{x}z)(\bar{y}z)(\overline{x^2-y^2})|-i|(yz)(xy)(x^2-y^2)|$
$+i\sqrt{3}|(yz)(xy)(z^2)|-|(xy)(xz)(x^2-y^2)|-\sqrt{3}|(xy)(xz)(z^2)|)/2\sqrt{3}$

TABLE 44--Continued

$(21) = (4|(\bar{x}z)(\bar{y}z)(x^2\bar{-}y^2)|-i|(yz)(xy)(x^2-y^2)|$

$-i\sqrt{3}|(xy)(yz)(z^2)|-|(xy)(xz)(x^2-y^2)|-\sqrt{3}|(xy)(xz)(z^2)|$

$-i|(yz)(\bar{x}y)(x^2\bar{-}y^2)|+i|(xy)(\bar{y}z)(x^2\bar{-}y^2)|+i|(\bar{x}y)(\bar{y}z)(x^2-y^2)|$

$+i\sqrt{3}|(yz)(\bar{x}y)(\bar{z}^2)|-i\sqrt{3}|(xy)(\bar{y}z)(\bar{z}^2)|-i\sqrt{3}|(x\bar{y})(\bar{y}z)(z^2)|$

$+|(xy)(\bar{x}z)(x^2\bar{-}y^2)|+|(\bar{x}y)(xz)(x^2\bar{-}y^2)|+|(\bar{x}y)(\bar{x}z)(x^2-y^2)|$

$+\sqrt{3}|(xy)(\bar{x}z)(\bar{z}^2)|+\sqrt{3}|(\bar{x}y)(xz)(\bar{z}^2)|+\sqrt{3}|(\bar{x}y)(\bar{x}z)(z^2)|)/4\sqrt{3}$

Γ_{8c}^{C}

$(1) = (2|(xy)(\bar{x}z)(\bar{y}z)|-|(\bar{x}y)(xz)(\bar{y}z)|-|(\bar{x}y)(\bar{x}z)(yz)|)/\sqrt{6}$

$(2) = (|(xy)(\bar{x}y)(x^2\bar{-}y^2)|+|(xz)(\bar{x}z)(x^2\bar{-}y^2)|+|(yz)(\bar{y}z)(x^2\bar{-}y^2)|)/\sqrt{3}$

$(3) = (2|(xy)(\bar{x}y)(x^2\bar{-}y^2)|-|(xz)(\bar{x}z)(x^2\bar{-}y^2)|-|(yz)(\bar{y}z)(x^2\bar{-}y^2)|$

$-\sqrt{3}|(xz)(\bar{x}z)(\bar{z}^2)|+\sqrt{3}|(yz)(\bar{y}z)(\bar{z}^2)|)/2\sqrt{3}$

$(4) = |(z^2)(\bar{z}^2)(x^2\bar{-}y^2)|$

$(5) = (i|(yz)(\bar{y}z)(xz)|-i|(xy)(\bar{x}y)(xz)|+|(xy)(\bar{x}y)(yz)|$

$-|(xz)(\bar{x}z)(yz)|)/2$

$(6) = (2i|(yz)(xy)(\bar{z}^2)|-i|(yz)(\bar{x}y)(z^2)|-i|(\bar{y}z)(xy)(z^2)|$

$+2i\sqrt{3}|(yz)(xy)(x^2\bar{-}y^2)|-i\sqrt{3}|(yz)(\bar{x}y)(x^2-y^2)|$

$-i\sqrt{3}|(\bar{y}z)(xy)(x^2-y^2)|+2|(xy)(xz)(\bar{z}^2)|-|(xy)(\bar{x}z)(z^2)|$

$-|(\bar{x}y)(xz)(z^2)|-2\sqrt{3}|(xy)(xz)(x^2\bar{-}y^2)|$

$+\sqrt{3}|(xy)(\bar{x}z)(x^2-y^2)|+\sqrt{3}|(\bar{x}y)(xz)(x^2-y^2)|)/4\sqrt{3}$

TABLE 44--Continued

$(7) \quad = (-|(xy)(\bar{x}z)(x^2-y^2)|+|(\bar{x}y)(xz)(x^2-y^2)|+\sqrt{3}|(\bar{x}y)(xz)(z^2)|$
$-\sqrt{3}|(xy)(\bar{x}z)(z^2)|-i|(yz)(\bar{x}y)(x^2-y^2)|+i|(\bar{y}z)(xy)(x^2-y^2)|$
$+i\sqrt{3}|(yz)(\bar{x}y)(z^2)|-i\sqrt{3}|(\bar{y}z)(xy)(z^2)|)/4$

$(8) \quad = (-2|(\bar{y}z)(z^2)(x^2-y^2)|+|(yz)(z^2)(x^2\bar{-}y^2)|+|(yz)(\bar{z}^2)(x^2-y^2)|$
$-2i|(\bar{x}z)(z^2)(x^2-y^2)|+i|(xz)(z^2)(x^2\bar{-}y^2)|+i|(xz)(\bar{z}^2)(x^2-y^2)|)/2\sqrt{3}$

$(9) \quad = (i|(xz)(z^2)(x^2\bar{-}y^2)|-i|(xz)(\bar{z}^2)(x^2-y^2)|$
$+i\sqrt{3}|(xz)(z^2)(\bar{z}^2)|-i\sqrt{3}|(xz)(x^2-y^2)(x^2\bar{-}y^2)|+|(yz)(z^2)(x^2\bar{-}y^2)|$
$-|(yz)(\bar{z}^2)(x^2-y^2)|+\sqrt{3}|(yz)(x^2-y^2)(x^2\bar{-}y^2)|-\sqrt{3}|(yz)(z^2)(\bar{z}^2)|)/4$

$(10) = (2i|(xz)(\bar{x}z)(\bar{x}y)|+2i|(yz)(\bar{y}z)(\bar{x}y)|+|(yz)(\bar{y}z)(xz)|$
$+|(xy)(\bar{x}y)(xz)|+i|(xy)(\bar{x}y)(yz)|+i|(xz)(\bar{x}z)(yz)|)/2\sqrt{3}$

$(11) = (8i|(\bar{x}z)(\bar{y}z)(x^2-y^2)|-4i|(\bar{x}z)(yz)(x^2\bar{-}y^2)|-4i|(xz)(\bar{y}z)(x^2\bar{-}y^2)|$
$+2|(yz)(xy)(x^2\bar{-}y^2)|-|(yz)(\bar{x}y)(x^2-y^2)|-|(\bar{y}z)(xy)(x^2-y^2)|$
$-2\sqrt{3}|(yz)(xy)(\bar{z}^2)|+\sqrt{3}|(yz)(\bar{x}y)(z^2)|+\sqrt{3}|(\bar{y}z)(xy)(z^2)|$
$+2i|(xy)(xz)(x^2\bar{-}y^2)|-i|(xy)(\bar{x}z)(x^2-y^2)|-i|(\bar{x}y)(xz)(x^2-y^2)|$
$+2i\sqrt{3}|(xy)(xz)(\bar{z}^2)|-i\sqrt{3}|(xy)(\bar{x}z)(z^2)|-i\sqrt{3}|(\bar{x}y)(xz)(z^2)|)/12$

$(12) = (-4i|(\bar{x}z)(yz)(\bar{z}^2)|+4i|(xz)(\bar{y}z)(\bar{z}^2)|-|(yz)(\bar{x}y)(z^2)|$
$+|(\bar{y}z)(xy)(z^2)|-\sqrt{3}|(yz)(\bar{x}y)(x^2-y^2)|+\sqrt{3}|(\bar{y}z)(xy)(x^2-y^2)|$
$-i|(xy)(\bar{x}z)(z^2)|+i|(\bar{x}y)(xz)(z^2)|+i\sqrt{3}|(xy)(\bar{x}z)(x^2-y^2)|$
$-i\sqrt{3}|(\bar{x}y)(xz)(x^2-y^2)|)/4\sqrt{3}$

TABLE 44--Continued

$(13) = (2i\,|(\overline{xy})(z^2)(\overline{z^2})|+2i\,|(\overline{xy})(x^2-y^2)(\overline{x^2-y^2})|+|(xz)(z^2)(\overline{z^2})|$

$+|(xz)(x^2-y^2)(\overline{x^2-y^2})|+i\,|(yz)(z^2)(\overline{z^2})|+i\,|(yz)(x^2-y^2)(\overline{x^2-y^2})|)/2\sqrt{3}$

$(14) = (4i\,|(\overline{xy})(z^2)(\overline{z^2})|-4i\,|(\overline{xy})(x^2-y^2)(\overline{x^2-y^2})|-|(xz)(z^2)(\overline{z^2})|$

$+|(xz)(x^2-y^2)(\overline{x^2-y^2})|+\sqrt{3}|(xz)(z^2)(\overline{x^2-y^2})|-\sqrt{3}|(xz)(\overline{z^2})(x^2-y^2)|$

$+i\,|(yz)(x^2-y^2)(\overline{x^2-y^2})|-i\,|(yz)(z^2)(\overline{z^2})|-i\sqrt{3}|(yz)(z^2)(\overline{x^2-y^2})|$

$+i\sqrt{3}|(yz)(\overline{z^2})(x^2-y^2)|)/4\sqrt{3}$

$(15) = (-|(\overline{xy})(\overline{xz})(yz)|-|(\overline{xy})(xz)(\overline{yz})|-|(xy)(\overline{xz})(\overline{yz})|)/\sqrt{3}$

$(16) = (-2i\,|(xz)(yz)(z^2)|+|(\overline{yz})(\overline{xy})(\overline{z^2})|+\sqrt{3}|(\overline{yz})(\overline{xy})(\overline{x^2-y^2})|$

$+i\,|(\overline{xy})(\overline{xz})(\overline{z^2})|-i\sqrt{3}|(\overline{xy})(\overline{xz})(\overline{x^2-y^2})|)/2\sqrt{3}$

$(17) = (4i\,|(xz)(yz)(z^2)|+|(\overline{yz})(\overline{xy})(\overline{z^2})|+\sqrt{3}|(\overline{yz})(\overline{xy})(\overline{x^2-y^2})|$

$+i\,|(\overline{xy})(\overline{xz})(\overline{z^2})|-i\sqrt{3}|(\overline{xy})(\overline{xz})(\overline{x^2-y^2})|+|(\overline{yz})(xy)(z^2)|$

$+|(yz)(\overline{xy})(z^2)|+|(yz)(xy)(\overline{z^2})|+\sqrt{3}|(yz)(xy)(\overline{x^2-y^2})|$

$+\sqrt{3}|(yz)(\overline{xy})(x^2-y^2)|+\sqrt{3}|(\overline{yz})(xy)(x^2-y^2)|-i\,|(\overline{xy})(xz)(z^2)|$

$-i\,|(xy)(\overline{xz})(z^2)|-i\,|(xy)(xz)(\overline{z^2})|+i\sqrt{3}|(\overline{xy})(xz)(x^2-y^2)|$

$+i\sqrt{3}|(xy)(\overline{xz})(x^2-y^2)|+i\sqrt{3}|(xy)(xz)(x^2-y^2)|)/4\sqrt{3}$

$(18) = (-i\,|(xy)(z^2)(x^2-y^2)|-|(\overline{xz})(\overline{z^2})(\overline{x^2-y^2})|-i\,|(\overline{yz})(\overline{z^2})(\overline{x^2-y^2})|)/\sqrt{3}$

$(19) = (2i\,|(xy)(z^2)(x^2-y^2)|-|(\overline{xz})(\overline{z^2})(\overline{x^2-y^2})|-i\,|(\overline{yz})(\overline{z^2})(\overline{x^2-y^2})|$

$-|(\overline{xz})(z^2)(x^2-y^2)|-|(xz)(\overline{z^2})(x^2-y^2)|-|(xz)(z^2)(\overline{x^2-y^2})|$

$+i\,|(\overline{yz})(z^2)(x^2-y^2)|+i\,|(yz)(\overline{z^2})(x^2-y^2)|+i\,|(yz)(z^2)(\overline{x^2-y^2})|)/2\sqrt{3}$

TABLE 44--Continued

$$\begin{aligned}
(20) = (&-2|(\bar{x}z)(\bar{y}z)(x^2-y^2)|-2|(\bar{x}z)(yz)(\overline{x^2-y^2})|-2|(xz)(\bar{y}z)(\overline{x^2-y^2})| \\
&-i|(\bar{y}z)(xy)(x^2-y^2)|-i|(yz)(\bar{x}y)(x^2-y^2)|-i|(yz)(xy)(\overline{x^2-y^2})| \\
&+i\sqrt{3}|(\bar{y}z)(xy)(z^2)|+i\sqrt{3}|(yz)(\bar{x}y)(z^2)|+i\sqrt{3}|(yz)(xy)(\bar{z}^2)| \\
&+|(\bar{x}y)(xz)(x^2-y^2)|+|(xy)(\bar{x}z)(x^2-y^2)|+|(xy)(xz)(\overline{x^2-y^2})| \\
&+\sqrt{3}|(\bar{x}y)(xz)(z^2)|+\sqrt{3}|(xy)(\bar{x}z)(z^2)|+\sqrt{3}|(xy)(xz)(\bar{z}^2)|)/6
\end{aligned}$$

$$\begin{aligned}
(21) = (&-4|(\bar{x}z)(\bar{y}z)(x^2-y^2)|-4|(\bar{x}z)(yz)(\overline{x^2-y^2})| \\
&-4|(xz)(\bar{y}z)(\overline{x^2-y^2})|+i|(\bar{y}z)(xy)(x^2-y^2)|+i|(yz)(\bar{x}y)(x^2-y^2)| \\
&+i|(yz)(xy)(\overline{x^2-y^2})|-i\sqrt{3}|(\bar{y}z)(xy)(z^2)|-i\sqrt{3}|(yz)(\bar{x}y)(z^2)| \\
&-i\sqrt{3}|(yz)(xy)(\bar{z}^2)|-|(\bar{x}y)(xz)(x^2-y^2)|-|(xy)(\bar{x}z)(x^2-y^2)| \\
&-|(xy)(xz)(\overline{x^2-y^2})|-\sqrt{3}|(\bar{x}y)(xz)(z^2)|-\sqrt{3}|(xy)(\bar{x}z)(z^2)| \\
&-\sqrt{3}|(xy)(xz)(\bar{z}^2)|-3i|(\bar{y}z)(\bar{x}y)(\overline{x^2-y^2})|+3i\sqrt{3}|(\bar{y}z)(\bar{x}y)(\bar{z}^2)| \\
&-3|(\bar{x}y)(\bar{x}z)(\overline{x^2-y^2})|-3\sqrt{3}|(\bar{x}y)(\bar{x}z)(\bar{z}^2)|)/12
\end{aligned}$$

TABLE 45

a) Numbering of the Eigenvectors of the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ Coupling Scheme for the Spin-Orbit Perturbation

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Γ_6^C

$(1) = {}^2A^C_{1g}((t_{2g})^2e_g)$

$(2) = {}^2T^C_{1g}((t_{2g})^3)$

$(3) = {}^2T^C_{1g}((t_{2g})^2({}^3T_{1g})e_g)$

$(4) = {}^2T^C_{1g}((t_{2g})^2({}^1T_{2g})e_g)$

$(5) = {}^2T^C_{1g}(t_{2g}(e_g)^2({}^3A_{2g}))$

$(6) = {}^2T^C_{1g}(t_{2g}(e_g)^2({}^1E_g))$

$(7) = {}^4T^C_{1g}((t_{2g})^2e_g)$

$(8) = {}^4T^C_{1g}(t_{2g}(e_g)^2)$

$(9) = {}^4T^C_{2g}((t_{2g})^2e_g)$

Γ_7^C

$(1) = {}^2A^C_{2g}((t_{2g})^2e_g)$

$(2) = {}^2T^C_{2g}((t_{2g})^3)$

$(3) = {}^2T^C_{2g}((t_{2g})^2({}^3T_{1g})e_g)$

$(4) = {}^2T^C_{2g}((t_{2g})^2({}^1T_{2g})e_g)$

$(5) = {}^2T^C_{2g}(t_{2g}(e_g)^2({}^1A_{1g}))$

$(6) = {}^2T^C_{2g}(t_{2g}(e_g)^2({}^1E_g))$

$(7) = {}^4T^C_{1g}((t_{2g})^2e_g)$

$(8) = {}^4T^C_{1g}(t_{2g}(e_g)^2)$

$(9) = {}^4T^C_{2g}((t_{2g})^2e_g)$

TABLE 45--Continued

Γ_8^C

$(1) = {}^2E_g^C((t_{2g})^3)$

$(2) = {}^2E_g^C((t_{2g})^2({}^1A_{1g})e_g)$

$(3) = {}^2E_g^C((t_{2g})^2({}^1E_g)e_g)$

$(4) = {}^2E_g^C((e_g)^3)$

$(5) = {}^2T_{1g}^C((t_{2g})^3)$

$(6) = {}^2T_{1g}^C((t_{2g})^2({}^3T_{1g})e_g)$

$(7) = {}^2T_{1g}^C((t_{2g})^2({}^1T_{2g})e_g)$

$(8) = {}^2T_{1g}^C(t_{2g}(e_g)^2({}^3A_{2g}))$

$(9) = {}^2T_{1g}^C(t_{2g}(e_g)^2({}^1E_g))$

$(10) = {}^2T_{2g}^C((t_{2g})^3)$

$(11) = {}^2T_{2g}^C((t_{2g})^2({}^3T_{1g})e_g)$

$(12) = {}^2T_{2g}^C((t_{2g})^2({}^1T_{2g})e_g)$

$(13) = {}^2T_{2g}^C(t_{2g}(e_g)^2({}^1A_{1g}))$

$(14) = {}^2T_{2g}^C(t_{2g}(e_g)^2({}^1E_g))$

$(15) = {}^4A_{2g}^C((t_{2g})^3)$

$(16) = (1){}^4T_{1g}^C((t_{2g})^2e_g)$

$(17) = (2){}^4T_{1g}^C((t_{2g})^2e_g)$

$(18) = (1){}^4T_{1g}^C(t_{2g}(e_g)^2)$

$(19) = (2){}^4T_{1g}^C(t_{2g}(e_g)^2)$

$(20) = (1){}^4T_{2g}^C((t_{2g})^2e_g)$

$(21) = (2){}^4T_{2g}^C((t_{2g})^2e_g)$

TABLE 45--Continued

b) The Non-Zero Matrix Elements (H'_{jk}'s) for the Spin-Orbit Perturbation of the $\{\chi^C, X^C, \Gamma^C, \Gamma^Q\}$ Coupling Scheme

Γ_6^C					
j	k	ζ	j	k	ζ
1	2	$3i/\sqrt{6}$	4	8	$i/\sqrt{2}$
1	3	$-i/\sqrt{6}$	4	9	$-1/\sqrt{8}$
1	5	$-i/\sqrt{6}$	5	5	$-1/3$
1	6	$-i/\sqrt{2}$	5	7	$-i/3\sqrt{2}$
1	8	$-2/\sqrt{3}$	5	8	$-i\sqrt{2}/3$
2	3	$-1/2$	5	9	$1/\sqrt{2}$
2	4	$1/2$	6	6	$-1/2$
2	7	$-i/\sqrt{2}$	6	7	$-2i/\sqrt{6}$
2	9	$-1/\sqrt{2}$	7	7	$-5/12$
3	3	$-1/3$	7	8	$-5/6$
3	4	$-1/2$	7	9	$-i/4$
3	5	$5/6$	8	8	$5/6$
3	6	$-1/\sqrt{3}$	8	9	$i/2$
3	7	$-i/6\sqrt{2}$	9	9	$1/4$
3	8	$-i/3\sqrt{2}$			
3	9	$-1/\sqrt{8}$			
4	5	$1/2$			
4	7	$i/\sqrt{8}$			

TABLE 45--*Continued*

Γ_7^C					
j	k	ζ	j	k	ζ
1	2	$-1/\sqrt{2}$	5	5	1
1	3	$1/\sqrt{6}$	5	7	$-3/\sqrt{6}$
1	5	$-1/\sqrt{2}$	5	9	$i/\sqrt{6}$
1	6	$1/\sqrt{2}$	6	6	$-1/2$
1	9	$-i/\sqrt{3}$	6	9	$2i/\sqrt{6}$
2	3	$-1/2\sqrt{3}$	7	7	$1/4$
2	4	$\sqrt{3}/2$	7	8	$1/2$
2	7	$-3/\sqrt{6}$	7	9	$i/4$
2	9	$i/\sqrt{6}$	8	8	$-1/2$
3	3	$-1/3$	8	9	$-i/2$
3	4	$1/2$	9	9	$-5/12$
3	5	$-1/2\sqrt{3}$			
3	6	$-1/\sqrt{3}$			
3	7	$1/\sqrt{8}$			
3	8	$-1/\sqrt{2}$			
3	9	$i/6\sqrt{2}$			
4	5	$\sqrt{3}/2$			
4	7	$-1/\sqrt{8}$			
4	8	$1/\sqrt{2}$			
4	9	$i/\sqrt{8}$			

TABLE 45--Continued

Γ_8^C

j	k	ζ	j	k	ζ
1	7	$3i/\sqrt{6}$	3	8	$i\sqrt{3}/6$
1	10	$-1/\sqrt{2}$	3	9	$i/2$
1	11	$-1/\sqrt{6}$	3	10	$1/2$
1	20	$-2i/\sqrt{6}$	3	11	$-1/2\sqrt{3}$
1	21	$-2i/\sqrt{6}$	3	13	$1/2$
2	6	$i/\sqrt{3}$	3	14	$-1/2$
2	8	$-i\sqrt{3}/6$	3	16	$\sqrt{3}/6$
2	9	$-i/2$	3	17	$\sqrt{3}/6$
2	10	-1	3	18	$-1/\sqrt{3}$
2	11	$1/\sqrt{3}$	3	19	$-1/\sqrt{3}$
2	13	$1/2$	3	20	$i/2\sqrt{3}$
2	14	$-1/2$	3	21	$i/2\sqrt{3}$
2	16	$1/\sqrt{3}$	4	8	$-i/2$
2	17	$1/\sqrt{3}$	4	9	$-i\sqrt{3}/2$
2	18	$1/\sqrt{3}$	4	13	$-\sqrt{3}/2$
2	19	$1/\sqrt{3}$	4	14	$-\sqrt{3}/2$
2	20	$-i/\sqrt{3}$	4	18	1
2	21	$-i/\sqrt{3}$	4	19	1
3	5	$i\sqrt{3}/2$	5	6	$1/4$
3	6	$i\sqrt{3}/6$	5	7	$-1/4$

TABLE 45--Continued

j	k	ζ	j	k	ζ
5	10	$i\sqrt{3}/2$	7	13	$-i\sqrt{3}/4$
5	11	$-i/4$	7	14	$-i\sqrt{3}/2$
5	12	$3i/4$	7	16	$-i/4$
5	16	$i/2$	7	17	$i/2$
5	17	$-i$	7	18	$-i/2$
5	20	$-1/2$	7	19	i
6	6	$1/6$	7	20	$-1/4$
6	7	$1/4$	8	8	$1/6$
6	8	$-5/12$	8	11	$-5i/4$
6	9	$1/2\sqrt{3}$	8	12	$-i/4$
6	10	$i\sqrt{3}/4$	8	16	$i/6$
6	11	$-i/2$	8	17	$-i/3$
6	12	$-i/4$	8	18	$i/3$
6	13	$i\sqrt{3}/4$	8	19	$-2i/3$
6	16	$i/12$	8	20	$1/2$
6	17	$-i/6$	9	9	$1/4$
6	18	$i/6$	9	12	$i\sqrt{3}/2$
6	19	$-i/3$	9	14	$3i/4$
6	20	$-1/4$	9	16	$i/\sqrt{3}$
7	8	$-1/4$	9	17	$-2i/\sqrt{3}$
7	10	$-i\sqrt{3}/4$	10	11	$1/4\sqrt{3}$
7	11	$i/4$	10	12	$-\sqrt{3}/4$

TABLE 45--Continued

j	k	ζ	j	k	ζ
10	15	-1	14	20	$i/\sqrt{3}$
10	16	$-\sqrt{3}/2$	14	21	$-2i/\sqrt{3}$
10	20	$i/2\sqrt{3}$	15	20	$i/\sqrt{3}$
10	21	$-1/\sqrt{3}$	15	21	$-2i/\sqrt{3}$
11	11	1/6	16	16	1/6
11	12	-1/4	16	17	1/6
11	13	$1/4\sqrt{3}$	16	18	1/3
11	14	$1/2\sqrt{3}$	16	19	1/3
11	15	$2/\sqrt{3}$	16	21	$-i/2$
11	16	1/4	17	17	-1/12
11	18	-1/2	17	18	1/3
11	20	$i/12$	17	19	-1/6
11	21	$-i/6$	17	20	$-i/2$
12	13	$-\sqrt{3}/4$	17	21	$-i/4$
12	16	-1/4	18	18	-1/3
12	18	1/2	18	19	-1/3
12	20	$i/4$	18	21	i
12	21	$-i/2$	19	19	1/6
13	13	-1/2	19	20	i
13	16	$-\sqrt{3}/2$	19	21	$i/2$
13	20	$i/2\sqrt{3}$	20	20	1/6
13	21	$-i/\sqrt{3}$	20	21	1/6
14	14	1/4	21	21	-1/12

The Axial Ligand Field

The cubic states decompose as shown in Table 37 when the symmetry is lowered to tetragonal.

The tetragonal wave functions are then readily obtained from Table 44. Again, after converting the wave functions into weak field microstate form the matrix elements for the axial ligand field perturbation can be readily calculated.

This last perturbation for the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme block diagonalizes the secular determinant into two 30 by 30's (Γ_6^Q and Γ_7^Q) as expected.

The non-zero matrix elements (the H'_{jk}'s) for the axial ligand field perturbation of the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme are given in Table 46. The complete energy matrices for this coupling scheme can then be obtained by appropriately superimposing the spin-orbit matrices (Γ_6^C, Γ_7^C and Γ_8^C from Table 45) and the cubic matrices (from Table 43) onto Γ_6^Q and Γ_7^Q from Table 46.

Checking of the Strong Field Perturbation Matrices

We have obtained the unitary transformation matrix between the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme and the $\{L, S, X^C, \Gamma^C, \Gamma^Q\}$ coupling scheme. The elements of this unitary transformation matrix are presented in Table 47.

We have checked the matrix elements of the strong field coupling scheme with those of the weak field coupling scheme using this unitary transformation matrix.

TABLE 46

a) Numbering of the Eigenvectors of the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ Coupling Scheme for the Axial Ligand Field Perturbation

Γ_6^Q

1 through 21 = 1 through 21 of Γ_{8a}^C

22 through 30 = 1 through 9 of Γ_6^C

Γ_7^Q

1 through 21 = 1 through 21 of Γ_{8c}^C

22 through 30 = 1 through 9 of Γ_7^C

b) The Non-Zero Matrix Elements (H'_{jk}'s) for the Axial Ligand Field Perturbation of the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ Coupling Scheme

Γ_6^Q

j	k	H'_{jk}	j	k	H'_{jk}
1	1	-7Dt	5	5	-7Dt
2	2	(6Ds+4Dt)/3	5	10	i(3Ds-5Dt)/$\sqrt{3}$
2	3	2(3Ds-5Dt)/3	6	6	(24Ds-19Dt)/12
2	22	-2(3Ds-5Dt)/3	6	11	-i(4Ds+5Dt)/4
3	3	-7Dt/6	6	24	(24Ds-5Dt)/6$\sqrt{2}$
3	22	-35Dt/6	7	7	-49Dt/12
4	4	-2Ds+8Dt	7	12	-i(4Ds+5Dt)/4

TABLE 46--Continued

j	k	H'_{jk}	j	k	H'_{jk}
7	25	-35Dt/6√2	17	28	-(24Ds-5Dt)/12
8	8	-(3Ds-19Dt)/3	17	30	-i(4Ds+5Dt)/4
8	26	-√2(3Ds-5Dt)/3	18	18	14Dt/3
9	9	-(3Ds-19Dt)/3	18	19	-(3Ds-5Dt)/3
9	13	i(4Ds+5Dt)/2	18	29	(3Ds-5Dt)/3
9	27	-√2(3Ds-5Dt)/3	19	19	14Dt/3
10	10	-7Dt	19	29	(3Ds-5Dt)/3
10	23	2i(3Ds-5Dt)/√6	20	20	-7Dt/6
11	11	7Dt/4	20	21	35Dt/12
11	24	-i(4Ds+5Dt)/√8	20	28	i(4Ds+5Dt)/4
12	12	-(8Ds+3Dt)/4	20	30	35Dt/12
12	25	-i(4Ds+5Dt)/√8	21	21	-7Dt/6
13	13	Ds+3Dt	21	28	i(4Ds+5Dt)/4
13	14	-(4Ds+5Dt)/2	21	30	-35Dt/12
13	27	i(4Ds+5Dt)/√2	22	22	-7Dt/6
14	14	Ds+3Dt	23	23	-7Dt
15	15	-7Dt	24	24	-7Dt/6
16	16	-7Dt/6	25	25	-7Dt/6
16	17	(24Ds-5Dt)/12	26	26	14Dt/3
16	21	-i(4Ds+5Dt)/4	27	27	14Dt/3
16	28	-(24Ds-5Dt)/12	28	28	-7Dt/6
16	30	i(4Ds+5Dt)/4	29	29	14Dt/3
17	17	-7Dt/6	30	30	-7Dt/6
17	20	-i(4Ds+5Dt)/4			

TABLE 46--Continued

Γ_7^Q

j	k	H'_{jk}	j	k	H'_{jk}
1	1	-7Dt	11	24	-35Dt/6√2
2	2	-(6Ds+11Dt)/3	12	12	(24Ds-19Dt)/12
2	3	-2(3Ds-5Dt)/3	12	25	(24Ds-5Dt)/6√2
2	22	2(3Ds-5Dt)/3	13	13	-(3Ds-19Dt)/3
3	3	-7Dt/6	13	14	(4Ds+5Dt)/2
3	22	(24Ds-5Dt)/6	13	26	-2(3Ds-5Dt)/3√2
4	4	2Ds+13Dt	13	27	(4Ds+5Dt)/√2
5	5	-7Dt	14	14	-(3Ds-19Dt)/3
5	10	-i(3Ds-5Dt)/√3	14	26	(4Ds+5Dt)/√2
5	23	2i(3Ds-5Dt)/√6	14	27	-√2(3Ds-5Dt)/3
6	6	-(8Ds+3Dt)/4	15	15	-7Dt
6	11	i(4Ds+5Dt)/4	16	16	-7Dt/6
6	24	-i(4Ds+5Dt)/√8	16	17	-(24Ds-5Dt)/12
7	7	7Dt/4	16	21	i(4Ds+5Dt)/4
7	12	i(4Ds+5Dt)/4	16	28	-(24Ds-5Dt)/12
7	25	-i(4Ds+5Dt)/√8	16	30	-i(4Ds+5Dt)/4
8	8	Ds+3Dt	17	17	-7Dt/6
9	9	Ds+3Dt	17	20	i(4Ds+5Dt)/4
9	13	-i(4Ds+5Dt)/2	17	28	(24Ds-5Dt)/12
9	26	i(4Ds+5Dt)/√2	17	30	-i(4Ds+5Dt)/4
10	10	-7Dt	18	18	14Dt/3
11	11	-49Dt/12	18	19	(3Ds-5Dt)/3

TABLE 46--Continued

j	k	H'_{jk}	j	k	H'_{jk}
18	29	(3Ds-5Dt)/3	22	22	-7Dt/6
19	19	14Dt/3	23	23	-7Dt
19	29	-(3Ds-5Dt)/3	24	24	-7Dt/6
20	20	-7Dt/6	25	25	-7Dt/6
20	21	-35Dt/12	26	26	14Dt/3
20	28	i(4Ds+5Dt)/4	27	27	14Dt/3
20	30	-35Dt/12	28	28	-7Dt/6
21	21	-7Dt/6	29	29	14Dt/3
21	28	-i(4Ds+5Dt)/4	30	30	-7Dt/6
21	30	-35Dt/12			

TABLE 47

The Elements of the Unitary Transformation Matrix Between the $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme and the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ Coupling Scheme

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The numbering of the eigenvectors used below is consistent with Table 45 for $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ and with Table 36 for $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$. The general form used below is

$$(\{x^C,X^C,\Gamma^C,\Gamma^Q\}) = \sum_i C_i(\{L,S,X^C,\Gamma^C,\Gamma^Q\})$$

where C_i is the appropriate constant.

$\Gamma_6{}^C$

$(1) = (1)$

$(2) = -(3i/\sqrt{35})(2)+(i/\sqrt{10})(3)+(\sqrt{30}/10)(4)+(i/\sqrt{7})(5)+(i/\sqrt{5})(6)$

$(3) = -(i/\sqrt{35})(2)+(2i/\sqrt{10})(3)-(2i/\sqrt{7})(5)$

$(4) = (3i/\sqrt{35})(2)-(i/\sqrt{10})(3)+(\sqrt{30}/10)(4)-(i/\sqrt{7})(5)+(i/\sqrt{5})(6)$

$(5) = -(2i/\sqrt{35})(2)-(i/\sqrt{10})(3)+(\sqrt{30}/10)(4)-(i/\sqrt{28})(5)+(3i/\sqrt{20})(6)$

$(6) = -(6i/\sqrt{105})(2)-(i\sqrt{30}/10)(3)+(1/\sqrt{10})(4)-(i\sqrt{21}/14)(5)-(i\sqrt{15}/10)(6)$

$(7) = (2i/\sqrt{5})(7)+(i/\sqrt{5})(8)$

$(8) = (i/\sqrt{5})(7)-(2i/\sqrt{5})(8)$

$(9) = -i(9)$

$\Gamma_7{}^C$

$(1) = i(1)$

$(2) = (1/\sqrt{2})(2)-(1/\sqrt{42})(3)-(i/\sqrt{6})(4)-(3/\sqrt{210})(5)-(2i/\sqrt{15})(6)$

$(3) = (2/\sqrt{14})(3)+(6/\sqrt{70})(5)-(i/\sqrt{5})(6)$

TABLE 47--Continued

$(4) = -(2/\sqrt{14})(3)+(i/\sqrt{2})(4)+(1/\sqrt{70})(5)-(i/\sqrt{5})(6)$

$(5) = (1/\sqrt{2})(2)+(1/\sqrt{42})(3)+(i/\sqrt{6})(4)+(3/\sqrt{210})(5)+(2i/\sqrt{15})(6)$

$(6) = -(4/\sqrt{42})(3)-(i/\sqrt{6})(4)+(9/\sqrt{210})(5)+(i/\sqrt{15})(6)$

$(7) = (2i/\sqrt{5})(7)+(i/\sqrt{5})(8)$

$(8) = (i/\sqrt{5})(7)-(2i/\sqrt{5})(8)$

$(9) = -i(9)$

Γ_8^C

$(1) = -(2/\sqrt{14})(2)+(6/\sqrt{70})(3)+(i/\sqrt{5})(4)$

$(2) = (\sqrt{3}/2)(1)+(1/\sqrt{28})(2)+(2/\sqrt{35})(3)-(i/\sqrt{10})(4)$

$(3) = (2/\sqrt{7})(2)+(1/\sqrt{35})(3)+(2i/\sqrt{10})(4)$

$(4) = (1/2)(1)-(3/\sqrt{84})(2)-(6/\sqrt{105})(3)+(3i/\sqrt{30})(4)$

$(5) = -(3i/\sqrt{35})(5)+(i/\sqrt{10})(6)+(\sqrt{30}/10)(7)+(i/\sqrt{7})(8)+(i/\sqrt{5})(9)$

$(6) = -(i/\sqrt{35})(5)+(2i/\sqrt{10})(6)-(2i/\sqrt{7})(8)$

$(7) = (3i/\sqrt{35})(5)-(i/\sqrt{10})(6)+(\sqrt{30}/10)(7)-(i/\sqrt{7})(8)+(i/\sqrt{5})(9)$

$(8) = -(2i/\sqrt{35})(5)-(i/\sqrt{10})(6)-(\sqrt{30}/10)(7)-(i/\sqrt{28})(8)+(3i/\sqrt{20})(9)$

$(9) = -(6i/\sqrt{105})(5)-(i\sqrt{30}/10)(6)+(1/\sqrt{10})(7)$

$-(3i/\sqrt{84})(8)-(i\sqrt{15}/10)(9)$

$(10) = (1/\sqrt{2})(10)-(1/\sqrt{42})(11)-(i/\sqrt{6})(12)-(3/\sqrt{210})(13)-(2i/\sqrt{15})(14)$

$(11) = (2/\sqrt{14})(11)+(6/\sqrt{70})(13)-(i/\sqrt{5})(14)$

$(12) = -(2/\sqrt{14})(11)+(i/\sqrt{2})(12)+(1/\sqrt{70})(13)-(i/\sqrt{5})(14)$

$(13) = (1/\sqrt{2})(10)+(1/\sqrt{42})(11)+(i/\sqrt{6})(12)+(3/\sqrt{210})(13)+(2i/\sqrt{15})(14)$

$(14) = -(4/\sqrt{42})(11)-(i/\sqrt{6})(12)+(9/\sqrt{210})(13)+(i/\sqrt{15})(14)$

TABLE 47--*Continued*

$(15) = -i(15)$

$(16) = (2i/\sqrt{5})(16)+(i/\sqrt{5})(18)$

$(17) = (2i/\sqrt{5})(17)+(i/\sqrt{5})(19)$

$(18) = (i/\sqrt{5})(16)-(2i/\sqrt{5})(18)$

$(19) = (i/\sqrt{5})(17)-(2i/\sqrt{5})(19)$

$(20) = -i(20)$

$(21) = -i(21)$

Making use of the diagonalization program we have compared the eigenvalues obtained from the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ strong field coupling scheme with those obtained from the $\{L, S, X^C, \Gamma^C, \Gamma^Q\}$ and $\{L, S, X^C, X^Q, \Gamma^Q\}$ weak field coupling schemes. For all identical sets of parameters tested the strong field scheme and the two weak field schemes yield identical eigenvalues. This is proof that the energy matrices are correct in the strong field and the weak field coupling schemes.

CHAPTER IV

THE PERCENT PURITIES OF THE EIGENFUNCTIONS IN THE VARIOUS COUPLING SCHEMES

The various coupling schemes for a given electronic configuration and symmetry yield identical eigenvalues for a given set of parameters when complete configuration interaction is included. But if we wish to consider the theory only to a first approximation, that is, to neglect all the off-diagonal matrix elements in the calculation of the eigenvalues, then the coupling schemes are no longer equivalent.

The percent purity is a measure of how much the off-diagonal elements contribute to a given level. Thus, a level that is 90 percent pure receives a contribution of 10 percent from the off-diagonal elements and a contribution of 90 percent from the diagonal element. With the inclusion of configuration interaction the eigenvalues and the percent purities of the eigenvectors are determined with the aid of a computer program.

An ideal coupling scheme would have all the levels 100 percent pure. Short of this, the closer the levels are, in a given scheme, to 100 percent pure the more accurate would be the description of the eigenfunctions in terms of the basis eigenvectors of that coupling scheme.

For a given eigenvalue the name (or label) attached to it reflects the parentage ascribed to the corresponding eigenvector in the coupling scheme being considered. For example, the label $\Gamma_6^Q\{^2E_g^Q(^2T_{1g}^C(^2F))\}$ from the $\{L,S,X^C,X^Q,\Gamma^Q\}$ coupling scheme implies that this Γ_6^Q level has, ultimately, ^2F as the parent. Now if the diagonal element in the secular determinant makes the greatest contribution to the eigenvalue then the label of the eigenvector, which is garnered from the diagonal element, reflects a reasonable parentage for the level. Conversely, if the diagonal element does not make the greatest contribution to the eigenvalue then the label, which is garnered from the diagonal element, no longer reflects a reasonable parentage for the level.

Obviously, then, construction of coupling schemes with high purities is of great importance.

The Percent Purities of the Cubic Levels

We shall consider the percent purities in three cubic coupling schemes; the $\{L,S,J\}$ weak field coupling scheme, the $\{L,S,X\}$ weak field coupling scheme and the $\{x^C,X^C,\Gamma^C\}$ strong field coupling scheme.

The order in which the perturbations are considered for these three schemes is given below

$\{L,S,J\}$: e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$, then V_c

$\{L,S,X\}$: e^2/r_{ij}, then V_c, then $\xi(r)\vec{\ell}\cdot\vec{s}$

$\{x^C,X^C\Gamma^C\}$: V_c, then e^2/r_{ij}, then $\xi(r)\vec{\ell}\cdot\vec{s}$

The {L,S,J} cubic weak field coupling scheme has been carried out by Ferguson[1] for d^3. We have carried out, and included in this report, the {L,S,X} weak field coupling scheme and the $\{x^C, X^C, \Gamma^C\}$ strong field coupling scheme for d^3 as parts of the tetragonal schemes described herein.

The {L,S,J} coupling scheme differs from the {L,S,X} and $\{x^C, X^C, \Gamma^C\}$ coupling schemes in that in the {L,S,J} scheme the spin-orbit interaction is considered as the second perturbation whereas in the other two cubic schemes the spin-orbit interaction is the third and last perturbation considered.

With the use of the diagonalization computer program we have determined the percent purities in these three coupling schemes for a series of $3d^3$ chromium (III) cubic complexes. The chromium (III) complexes considered are the hexachloro-, the hexaaquo-, the hexaammine- and the hexacyano-. Also, we have determined the percent purities in these three coupling schemes for a $3d^7$ cobalt (II) cubic complex. The cobalt (II) complex considered is the hexaammine-. The ligand field and Racah parameters for these complexes are given in Table 48.

For each chromium (III) complex, we considered values of 0 and 250 cm^{-1} for the spin-orbit parameter zeta while holding the other parameters constant. For the cobalt (II) complex, we considered values of 0, 250 and 500 cm^{-1} for the spin-orbit

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[1] J. Ferguson, Aust. J. Chem., 23, 635(1970), (d^3 and d^7).

TABLE 48

The Cubic Ligand Field and Racah Parameters[j,k] for $CrCl_6^{-3}$, $Cr(H_2O)_6^{+3}$, $Cr(NH_3)_6^{+3}$, $Cr(CN)_6^{-3}$ and $Co(NH_3)_6^{+2}$

Complex	Dq(cm^{-1})	B(cm^{-1})	C/B
$CrCl_6^{-3}$	1360	510	4.0
$Cr(H_2O)_6^{+3}$	1740	750	4.0
$Cr(NH_3)_6^{+3}$	2160	670	4.0
$Cr(CN)_6^{-3}$	2630	520	4.0
$Co(NH_3)_6^{+2}$	1100	740	4.0

[j] For the chromium (III) complexes: Hans Schläfer and Gunter Gliemann, Basic Principles of Ligand Field Theory, Wiley-Interscience, New York, 1969.

[k] For the cobalt (II) complex: B. N. Figgis, Introduction to Ligand Fields, Interscience Publishers, New York, 1966.

parameter zeta while holding the other parameters constant. This was done for each of the three cubic coupling schemes.

For the free ion,[1] chromium (III), zeta has a value of about 270 cm^{-1}. For the free ion,[2] cobalt (II), zeta has a value of about 570 cm^{-1}.

In Table 49 the average purities of the doublet and quartet levels for the three coupling schemes are given.

The $\{x^C, X^C, \Gamma^C\}$ strong field coupling scheme is found to yield the purest levels of the three coupling schemes considered. For each of the five complexes when zeta is zero the quartet levels of $\{x^C, X^C, \Gamma^C\}$ are, on the average, over 90 percent pure. The doublet levels of $\{x^C, X^C, \Gamma^C\}$ are, on the average, over 80 percent pure when zeta is zero. The only exception being the doublet levels of $Co(NH_3)_6^{+2}$ where the average purities dip to 72 percent. This is not surprising since for this d^7 complex the Dq value, which is diagonalized in $\{x^C, X^C, \Gamma^C\}$, is fairly small (1100 cm^{-1}). Even when zeta is given a non-zero value the $\{x^C, X^C, \Gamma^C\}$ levels stay, for the most part, well over 80 percent pure.

The levels in the $\{L,S,X\}$ weak field coupling scheme are found to be significantly purer than the levels in the $\{L,S,J\}$ weak field coupling scheme when zeta is zero. This is true for each of the five complexes considered. When zeta is given a non-zero

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[1] Hans Schläfer and Gunter Gliemann, *Basic Principles of Ligand Field Theory*, Wiley-Intersicence, New York, 1969.

[2] Ibid.

TABLE 49

The Average Percent Purities of the Eigenfunctions for the Cubic Levels in the {L,S,X}, {L,S,J} and $\{x^C, X^C, \Gamma^C\}$ $d^{3,7}$ Coupling Schemes

a) $CrCl_6^{-3}$

Average purities for the doublet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	48	31	83
250	47	29	83

Average purities for the quartet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	71	40	95
250	64	41	86

b) $Cr(H_2O)_6^{+3}$

Average purities for the doublet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	48	31	82
250	48	30	81

Average purities for the quartet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	71	42	93
250	64	42	83

TABLE 49--Continued

c) $Cr(NH_3)_6^{+3}$

Average purities for the doublet levels:

Zeta	$\{L,S,X\}$	$\{L,S,J\}$	$\{x^C,X^C,\Gamma^C\}$
0	47	28	85
250	46	27	85

Average purities for the quartet levels:

0	74	38	97
250	68	39	88

d) $Cr(CN)_6^{-3}$

Average purities for the doublet levels:

Zeta	$\{L,S,X\}$	$\{L,S,J\}$	$\{x^C,X^C,\Gamma^C\}$
0	44	24	87
250	41	28	87

Average purities for the quartet levels:

0	80	43	99
250	73	37	90

TABLE 49--Continued

e) $Co(NH_3)_6^{+2}$

Average purities for the doublet levels:

Zeta	$\{L,S,\chi\}$	$\{L,S,J\}$	$\{x^C,\chi^C,\Gamma^C\}$
0	51	40	72
250	50	41	70
500	50	43	69

Average purities for the quartet levels:

0	97	63	97
250	89	63	89
500	90	64	90

value the gap between $\{L,S,X\}$ and $\{L,S,J\}$ closes slightly but $\{L,S,X\}$ remains purer.

In Table 50 the fractions of the doublet and quartet levels for which the diagonal element makes the greatest contribution to the eigenvalue are listed. There are 26 doublet and 13 quartet levels for this electronic configuration and symmetry. Thus, when in Table 50 we list, say, 18-26 for the doublets of a given scheme we mean that for 18 of the 26 doublet levels the diagonal element makes the largest contribution to the eigenvalue.

Virtually all of the levels, both doublet and quartet, of the $\{x^C,X^C,\Gamma^C\}$ strong field coupling scheme receive the major contribution from the diagonal element in the secular determinant. This means that the labels derived in this strong field coupling scheme are appropriate.

All of the quartet levels of the $\{L,S,X\}$ weak field coupling scheme receive the major contribution from the diagonal element in the secular determinant. A majority, but by no means all, of the doublet levels of $\{L,S,X\}$ receive the major contribution from the diagonal element in the secular determinant. Thus, the quartet labels derived in this $\{L,S,X\}$ weak field coupling scheme are appropriate. However, the labelling for the doublet levels in this scheme breaks down somewhat.

For the $\{L,S,J\}$ weak field coupling scheme about half the levels, both doublet and quartet, receive the major contribution from the diagonal element in the secular determinant. This demonstrates a serious deficiency in this $\{L,S,J\}$ weak field

TABLE 50

The Fractions of the Levels in the {L,S,X}, {L,S,J} and $\{x^C, X^C, \Gamma^C\}$ Coupling Schemes for Which the Diagonal Element in the Secular Determinant Makes the Greatest Contribution to the Eigenvalue

a) $CrCl_6^{-3}$

Fractions for the doublet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	19-26	11-26	26-26
250	18-26	10-26	26-26

Fractions for the quartet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	13-13	6-13	13-13
250	13-13	5-13	13-13

b) $Cr(H_2O)_6^{+3}$

Fractions for the doublet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	18-26	11-26	26-26
250	18-26	12-26	26-26

Fractions for the quartet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C, X^C, \Gamma^C\}$
0	13-13	7-13	13-13
250	13-13	6-13	13-13

TABLE 50--*Continued*

c) $Cr(NH_3)_6^{+3}$

Fractions for the doublet levels:

Zeta	$\{L,S,X\}$	$\{L,S,J\}$	$\{x^C,X^C,\Gamma^C\}$
0	17-26	7-26	26-26
250	17-26	7-26	26-26

Fractions for the quartet levels:

0	13-13	7-13	13-13
250	13-13	7-13	13-13

d) $Cr(CN)_6^{-3}$

Fractions for the doublet levels:

Zeta	$\{L,S,X\}$	$\{L,S,J\}$	$\{x^C,X^C,\Gamma^C\}$
0	15-26	7-26	26-26
250	14-26	9-26	26-26

Fractions for the quartet levels:

0	13-13	7-13	13-13
250	13-13	6-13	13-13

TABLE 50--Continued

e) $Co(NH_3)_6^{+2}$

Fractions for the doublet levels:

Zeta	{L,S,X}	{L,S,J}	$\{x^C,X^C,\Gamma^C\}$
0	19-26	19-26	24-26
250	18-26	19-26	24-26
500	18-26	19-26	24-26

Fractions for the quartet levels:

0	13-13	9-13	13-13
250	13-13	10-13	13-13
500	13-13	10-13	13-13

coupling scheme since many of the labels derived in this scheme are not appropriate.

Four of the complexes we have considered have a central ion with an electronic configuration of $3d^3$. These four complexes offer a representative cross-section of Dq and B values. Dq varying from 1360 cm^{-1}, for $CrCl_6^{-3}$, to 2630 cm^{-1}, for $Cr(CN)_6^{-3}$. B varying from 510 cm^{-1}, for $CrCl_6^{-3}$, to 750 cm^{-1}, for $Cr(H_2O)_6^{+3}$. Therefore, we can say, in general, based on the purities, that the $\{x^C, X^C, \Gamma^C\}$ strong field coupling scheme is the most appropriate scheme for $3d^3$.

For the one $3d^7$ complex we have considered, $Co(NH_3)_6^{+2}$, the same trend as obtained for the chromium (III) complexes in relative purities for the three coupling schemes is observed.

The energy matrices that we have calculated are for d^3 electronic configuration. To apply these matrices to a d^7 electronic configuration it is necessary to change the sign of all parameters except the interelectronic repulsion parameters (B and C). The interelectronic repulsion parameters need not be changed in going from d^3 to d^7 electronic configuration because three holes (i.e., in d^7) will repel each other exactly as would three electrons.

Nonetheless, the weak field approach remains important despite the superiority demonstrated by the strong field approach for the complexes we have considered. First, from a didactic standpoint, it is often desirable to begin a consideration of the ligand field effect by starting with the free ion Russell-Saunders LS terms and observing how these terms are split (perturbed) by the ligand field. Of course, this sequence of perturbations is the weak field approach. Second, although we have considered a representative set of complexes there may be other complexes in which the interelectronic repulsions become more important than the ligand field. If the interelectronic repulsions do become more important than the ligand field then the weak field approach will be more advantageous than the strong field approach.

Inclusion of the spin-orbit interaction as the last perturbation considered, as is done in both the $\{L,S,X\}$ weak field scheme and the $\{x^C,X^C,\Gamma^C\}$ strong field scheme, yields significantly higher purities and better labelling than does inclusion of the spin-orbit interaction earlier in the sequence, as is done in the $\{L,S,J\}$ weak field scheme.

The Percent Purities of the Tetragonal Levels

We shall consider the percent purities in four tetragonal coupling schemes: the $\{L,S,X^C,X^Q,\Gamma^Q\}$ weak field coupling scheme, the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ weak field coupling scheme, the $\{x^C,X^C,X^Q,\Gamma^Q\}$ strong field coupling scheme and the $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ strong field coupling scheme.

The order in which the perturbations are considered for these four tetragonal coupling schemes is given in Tables 2 and 3.

The $\{L,S,X^C,X^Q,\Gamma^Q\}$, $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ coupling schemes have been presented in this report. The

$\{x^C, X^C, X^Q, \Gamma^Q\}$ coupling scheme has been recently devised by Perumareddi.[1]

In both the $\{L, S, X^C, X^Q, \Gamma^Q\}$ weak field coupling scheme and the $\{x^C, X^C, X^Q, \Gamma^Q\}$ strong field coupling scheme the spin-orbit interaction is the fourth and last perturbation considered. In the other two coupling schemes, the $\{L, S, X^C, \Gamma^C, \Gamma^Q\}$ weak field and the $\{x^C, X^C, \Gamma^C, \Gamma^Q\}$ strong field, the spin-orbit interaction is the penultimate perturbation considered. Thus, we can study what effect the position of the spin-orbit interaction in the sequence of perturbations has on the purities of the levels. Also, we can compare the purities of the levels in the strong field approach relative to the weak field approach.

With the use of the diagonalization computer program we have determined the percent purities in the four coupling schemes for a series of tetragonal complexes.

We will consider three tetragonal complexes with chromium (III) as the central ion for d^3 electronic configuration and two tetragonal complexes with cobalt (II) as the central ion for d^7 electronic configuration. The first two tetragonal chromium (III) complexes are based on $Cr(CN)_6^{-3}$. That is, we will assume the Dq, B and C values of the hexacyano-complex[2] while assigning non-zero values to the axial ligand field parameters Dt and Ds. For a weak tetragonal field we set Dt equal to $-100\ cm^{-1}$ and Ds equal to $100\ cm^{-1}$. For a strong tetragonal field we set Dt equal to $-600\ cm^{-1}$ and Ds equal to $600\ cm^{-1}$. The last tetragonal chromium (III) complex considered will be trans-difluorobis-(ethylenediamine)-chromium (III) perchlorate. This complex has been well-studied and the parameters unambiguously assigned.[1] The two tetragonal cobalt (II) complexes considered are based on $Co(NH_3)_6^{+2}$. Thus, we assume the Dq, B and C values of the hexaammine-complex[2] while assigning non-zero values to the axial ligand field parameters Dt and Ds. As for chromium (III), for a weak tetragonal field we set Dt equal to $-100\ cm^{-1}$ and Ds equal to $100\ cm^{-1}$. For a strong tetragonal field we set Dt equal to $-600\ cm^{-1}$ and Ds equal to $600\ cm^{-1}$.

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[1] J. R. Perumareddi, to be published.

[2] Hans Schläfer and Gunter Gliemann, Basic Principles of Ligand Field Theory, Wiley-Interscience, New York, 1969.

For the chromium (III) tetragonal complexes we consider values of 0 and $250\ cm^{-1}$ for the spin-orbit parameter zeta. For the cobalt (II) tetragonal complexes we consider values of 0, $250\ cm^{-1}$ and $500\ cm^{-1}$ for the spin-orbit parameter zeta.

In Table 51 the average purities of the doublet and quartet levels for the four coupling schemes are given.

For each of the chromium (III) complexes considered the $\{x^C, X^C, X^Q, \Gamma^Q\}$ strong field coupling scheme yields the purest levels. When the spin-orbit parameter zeta is zero the quartet levels in

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[1] L. Dubicki, M. Hitchman and P. Day, Inorg. Chem., 9, 188(1970).

[2] B. N. Figgis, Introduction to Ligand Fields, Interscience Publishers, New York, 1966.

TABLE 51

The Average Percent Purities of the Eigenfunctions for the Tetragonal Levels in the $\{L,S,X^C,X^Q,\Gamma^Q\}$, $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$, $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ d^3 Coupling Schemes

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a) Chromium (III) - Weak Tetragonal Field[j]
Dq = 2630 cm^{-1}, B = 520 cm^{-1}, C/B = 4.0,
Dt = -100 cm^{-1}, Ds = 100 cm^{-1}

Average purities for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	42	35	86	72
250	38	32	83	71

Average purities for the quartet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	80	45	98	47
250	79	36	97	42

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b) Chromium (III) - Strong Tetragonal Field[j]
Dq = 2630 cm^{-1}, B = 520 cm^{-1}, C/B = 4.0,
Dt, -600 cm^{-1}, Ds = 600 cm^{-1}

Average purities for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	39	32	78	72
250	38	30	75	60

TABLE 51--Continued

Average purities for the quartet levels:

0	79	45	98	47
250	73	36	88	40

c) Trans-$[Cr(en)_2F_2]^+$

$Dq = 2170\ cm^{-1}$, $B = 700\ cm^{-1}$, $C/B = 4.635$,

$Dt = -360\ cm^{-1}$, $Ds = 780\ cm^{-1}$

Average purities for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{X^C,X^C,X^Q,\Gamma^Q\}$	$\{X^C,X^C,\Gamma^C,\Gamma^Q\}$
0	42	37	77	60
250	41	36	74	58

Average purities for the quartet levels:

0	75	41	94	53
250	70	34	86	39

d) Cobalt (II) - Weak Tetragonal Field[k]

$Dq = 1100\ cm^{-1}$, $B = 740\ cm^{-1}$, $C/B = 4.0$,

$Dt = -100\ cm^{-1}$, $Ds = 100\ cm^{-1}$

Average purities for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{X^C,X^C,X^Q,\Gamma^Q\}$	$\{X^C,X^C,\Gamma^C,\Gamma^Q\}$
0	50	40	70	59

TABLE 51--Continued

250	44	41	62	57
500	42	40	60	57
Average purities for the quartet levels:				
0	97	54	97	51
250	92	47	92	47
500	79	61	78	61

e) Cobalt (II) - Strong Tetragonal Field[k]
Dq = 1100 cm^{-1}, B = 740 cm^{-1}, C/B = 4.0,
Dt = -600 cm^{-1}, Ds = 600 cm^{-1}

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	58	43	57	46
250	50	40	50	43
500	48	39	47	41
Average purities for the quartet levels:				
0	98	49	94	48
250	91	46	86	45
500	84	49	81	44

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[j] The parameters Dq, B and C are based on $Cr(CN)_6^{-3}$.

[k] The parameters Dq, B and C are based on $Co(NH_3)_6^{+2}$.

$\{x^C,X^C,X^Q,\Gamma^Q\}$ are well over 90% pure on the average and the doublet levels over 75% pure for each of the chromium (III) complexes considered. When zeta is given a non-zero value the quartet levels in $\{x^C,X^C,X^Q,\Gamma^Q\}$ remain well over 80% pure on the average and the doublet levels well over 70% pure for each of the chromium (III) complexes considered.

The doublet levels in the two strong field coupling schemes are found to be much purer than the doublet levels in the two weak field coupling schemes for the chromium (III) complexes considered. The $\{L,S,X^C,X^Q,\Gamma^Q\}$ weak field coupling scheme yields quartet levels which are well over 70% pure on the average both when zeta is 0 and 250 cm^{-1}. The quartet levels in both the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ weak field scheme and the $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ strong field scheme are less than 50% pure, on the average, when zeta is 0 and when zeta is 250 cm^{-1}.

In summary for the chromium (III) complexes that we have studied the observations are: (1) for the quartet levels it is the schemes that have the spin-orbit interaction as the last perturbation (i.e., $\{L,S,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,X^Q,\Gamma^Q\}$ which yield higher purities and (2) for the doublet levels it is the strong field schemes (i.e., $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$) which yield higher purities.

For the cobalt (II) complexes the $\{L,S,X^C,X^Q,\Gamma^Q\}$ weak field coupling scheme yields levels with purities comparable to those of the $\{x^C,X^C,X^Q,\Gamma^Q\}$ strong field coupling scheme. For the strong tetragonal field of cobalt (II) the levels, both doublet and quartet, in $\{L,S,X^C,X^Q,\Gamma^Q\}$ actually become slightly purer than those in $\{x^C,X^C,X^Q,\Gamma^Q\}$.

The levels in the $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ weak field scheme and the $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ strong field scheme, in which the spin-orbit interaction is the penultimate perturbation considered, are for the most part much less pure for the cobalt (II) complexes than are the levels in the $\{L,S,X^C,X^Q,\Gamma^Q\}$ weak field scheme and the $\{x^C,X^C,X^Q,\Gamma^Q\}$ strong field scheme, in which the spin-orbit interaction is the last perturbation considered.

In summary for the cobalt (II) complexes that we have studied the observations are: (1) for the quartet levels it is the schemes that have the spin-orbit interaction as the last perturbation (i.e., $\{L,S,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,X^Q,\Gamma^Q\}$) which yield higher purities, (2) for the doublet levels in a weak axial field the strong field schemes (i.e., $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$) yield somewhat higher purities than the weak field schemes and (3) for the doublet levels in a strong axial field it is the $\{L,S,X^C,X^Q,\Gamma^Q\}$ weak field scheme which yields the purest levels.

We find that for the quartet levels the observations, based on the purities, for chromium (III) and cobalt (II) are the same. For the doublet levels we find that the weak field schemes do better based on the purities, in comparison to the strong field schemes, for cobalt (II) than they do for chromium (III).

In Table 52 the fractions of the doublet and quartet levels for which the diagonal element makes the greatest contribution to the

TABLE 52

The Fractions of the Levels in the $\{L,S,X^C,X^Q,\Gamma^Q\}$ $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$, $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ d^3 Coupling Schemes for Which the Diagonal Element in the Secular Determinant Makes the Greatest Contribution to the Eigenvalue

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a) Chromium (III) - Weak Tetragonal Field[j]
$Dq = 2630\ cm^{-1}$, $B = 520\ cm^{-1}$, $C/B = 4.0$,
$Dt = -100\ cm^{-1}$, $Ds = 100\ cm^{-1}$

Fractions for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	21-40	24-40	40-40	40-40
250	20-40	20-40	40-40	38-48

Fractions for the quartet levels:

0	20-20	20-20	20-20	16-20
250	20-20	9-20	20-20	9-20

b) Chromium (III) - Strong Tetragonal Field[j]
$Dq = 2630\ cm^{-1}$, $B = 520\ cm^{-1}$, $C/B = 4.0$,
Dt = -600 cm-1, DS = $600\ cm^{-1}$

Fractions for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	19-40	20-40	39-40	40-40
250	19-40	19-40	38-40	32-40

TABLE 52--Continued

Fractions for the quartet levels:

0	20-20	20-20	20-20	16-20
250	20-20	9-20	19-20	9-20

c) Trans-$[Cr(en)_2F_2]^+$
Dq = 2170 cm^{-1}, B = 700 cm^{-1}, C/B = 4.635,
Dt = -360 cm^{-1}, DS = 780 cm^{-1}

Fractions for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	23-40	24-40	40-40	34-40
250	22-40	24-40	39-40	33-40

Fractions for the quartet levels:

0	20-20	13-20	20-20	20-20
250	20-20	8-20	20-20	8-20

d) Cobalt (II) - Weak Tetragonal Field[k]
Dq = 1100 cm^{-1}, B = 740 cm^{-1}, C/B = 4.0,
Dt = -100 cm^{-1}, Ds = 100 cm^{-1}

Fractions for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	28-40	26-40	37-40	37-40
250	28-40	29-40	33-40	36-40
500	29-40	27-40	35-40	32-40

TABLE 52--Continued

Fractions for the quartet levels:

0	20-20	20-20	20-20	18-20
250	20-20	11-20	20-20	11-20
500	20-20	18-20	20-20	18-20

e) Cobalt (II) - Strong Tetragonal Field[k]
$Dq = 1100\ cm^{-1}$, $B = 740\ cm^{-1}$, $C/B = 4.0$,
$Dt = -600\ cm^{-1}$, $Ds = 600\ cm^{-1}$

Fractions for the doublet levels:

Zeta	$\{L,S,X^C,X^Q,\Gamma^Q\}$	$\{L,S,X^C,\Gamma^C,\Gamma^Q\}$	$\{x^C,X^C,X^Q,\Gamma^Q\}$	$\{x^C,X^C,\Gamma^C,\Gamma^Q\}$
0	35-40	29-40	29-40	31-40
250	33-40	27-40	28-40	27-40
500	33-40	26-40	29-40	26-40

Fractions for the quartet levels:

0	20-20	17-20	20-20	18-20
250	20-20	13-20	19-20	14-20
500	20-20	13-20	20-20	13-20

[j] The parameters Dq, B and C are based on $Cr(CN)_6^{-3}$.

[k] The parameters Dq, B and C are based on $Co(NH_3)_6^{+2}$.

eigenvalue are listed. There are 40 doublet and 20 quartet levels for this electronic configuration and symmetry.

In summary, based on the fractions of the levels which receive the greatest contribution to the eigenvalue from the diagonal element, we find that: (1) for the quartet levels of both chromium (III) and cobalt (II) it is the schemes that have the spin-orbit interaction as the last perturbation (i.e., $\{L,S,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,X^Q,\Gamma^Q\}$ which yield the more appropriate labels, (2) for the doublet levels of chromium (III) it is the strong field schemes (i.e., $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$) which yield the more appropriate labels, (3) for the doublet levels of cobalt (II) in a weak axial field it is the strong field schemes (i.e., $\{x^C,X^C,X^Q,\Gamma^Q\}$ and $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$) which yield the more appropriate labels, and (4) for the doublet levels of cobalt (II) in a strong axial field it is the weak field schemes (i.e., $\{L,S,X^C,X^Q,\Gamma^Q\}$ and $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$) which yield the more appropriate labels.

The tetragonal complexes we have studied present a wide range of parameters. It is demonstrated, then, that the tetragonal coupling schemes which take the spin-orbit interaction as the last perturbation in the sequence yield purer levels and as good or better labelling of the eigenfunctions than do the tetragonal coupling schemes which take the spin-orbit interaction as the penultimate perturbation in the sequence. This is clearly indicated by comparing either $\{L,S,X^C,X^Q,\Gamma^Q\}$ with $\{L,S,X^C,\Gamma^C,\Gamma^Q\}$ or $\{x^C,X^C,X^Q,\Gamma^Q\}$ with $\{x^C,X^C,\Gamma^C,\Gamma^Q\}$ on the basis of purities (Table 51) and on the basis of the fractions of the levels for which the eigenvalue receives the greatest contribution from the diagonal element in the secular determinant (Table 52).

It is also demonstrated that the strong field approach is often favored over the weak field approach (cf., the chromium (III) complexes in Tables 51 and 52). Nonetheless, as Dq becomes small the weak field approach yields levels as pure and as good of labelling as the strong field approach (cf., the cobalt (II) complexes in Tables 51 and 52).

CHAPTER V

APPLICATIONS TO SOME TETRAGONAL CHROMIUM (III) COMPLEXES

To the low energy side of the lowest energy spin-allowed transition in a tetragonal chromium (III) complex there are expected five spin-forbidden (quartet-doublet) transitions. It is these five intraconfigurational doublets that we will be primarily concerned with. The five lowest energy doublet states expected for tetragonal chromium (III) and the quartet ground state are shown in Figure 12. The quartet ground state splits into two spin-orbital levels with an energy difference of at most a few wave numbers. The transition corresponding to this ground state splitting lies far outside the range in which we are interested.

The relative energy order of these five doublet states is dependent, primarily, on the axial ligand field parameters Dt and Ds, on the interelectronic repulsion parameters B and on the spin-orbit parameter ζ . Since each of these five doublet states (and the quartet ground state as well) arise from the same strong field configuration, $(t_{2g})^3$, the relative energy order of these doublet states is independent of the cubic ligand field parameter Dq. The dependence of these doublet states on the interelectronic repulsion parameter C is about the same.

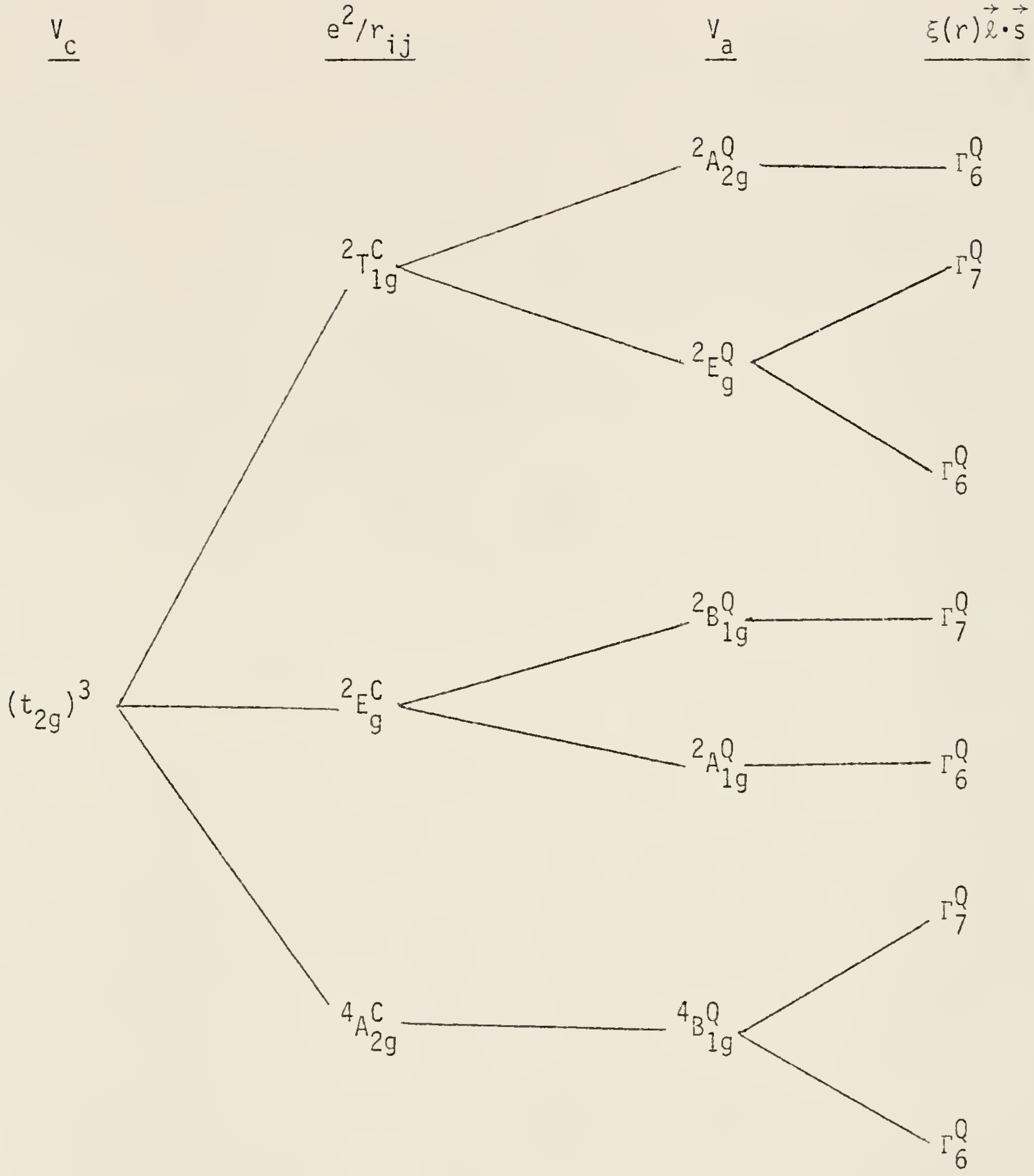

Figure 12. The Quartet Ground State and the Five Lowest Doublet States Expected for a Tetragonal Chromium (III) Complex.

The identification and assignment of the absorption bands which correspond to these and other spin-forbidden transitions is a difficult experimental task. These bands are very low in intensity. Furthermore, these bands generate a myriad of vibrational side bands, most with intensities of comparable magnitude to the electronic origins themselves.

If the electronic origins which correspond to the quartet-doublet transitions can be identified, then much useful information pertaining to the evaluation of the ligand field parameters can be obtained. Ultimately, this information can be used to help in better understanding the bonding in the complexes being studied.

However, before the spin-forbidden spectra can be used in the evaluation of parameters some knowledge of the spin-allowed spectra is essential.

For a tetragonal d^3 complex there are, with the spin-orbit interaction neglected, six spin-allowed transitions. These six lowest energy quartet states and the quartet ground state are shown in Figure 13. If the four lowest energy spin-allowed transitions (i.e., the transitions to the tetragonally split components of ${}^4T_{2g}^C$ and ${}^4T_{1g}^C$) are identified and assigned, then the ligand field parameters Dq, B, Dt and Ds can be evaluated unambiguously. The parameters are evaluated by an exact fit of the observed transitions using the calculated energy levels.

If Dq, B, Dt and Ds are evaluated from the spin-allowed spectra, then the following information can be obtained by fitting the five lowest energy spin-forbidden transitions. First, the fitting

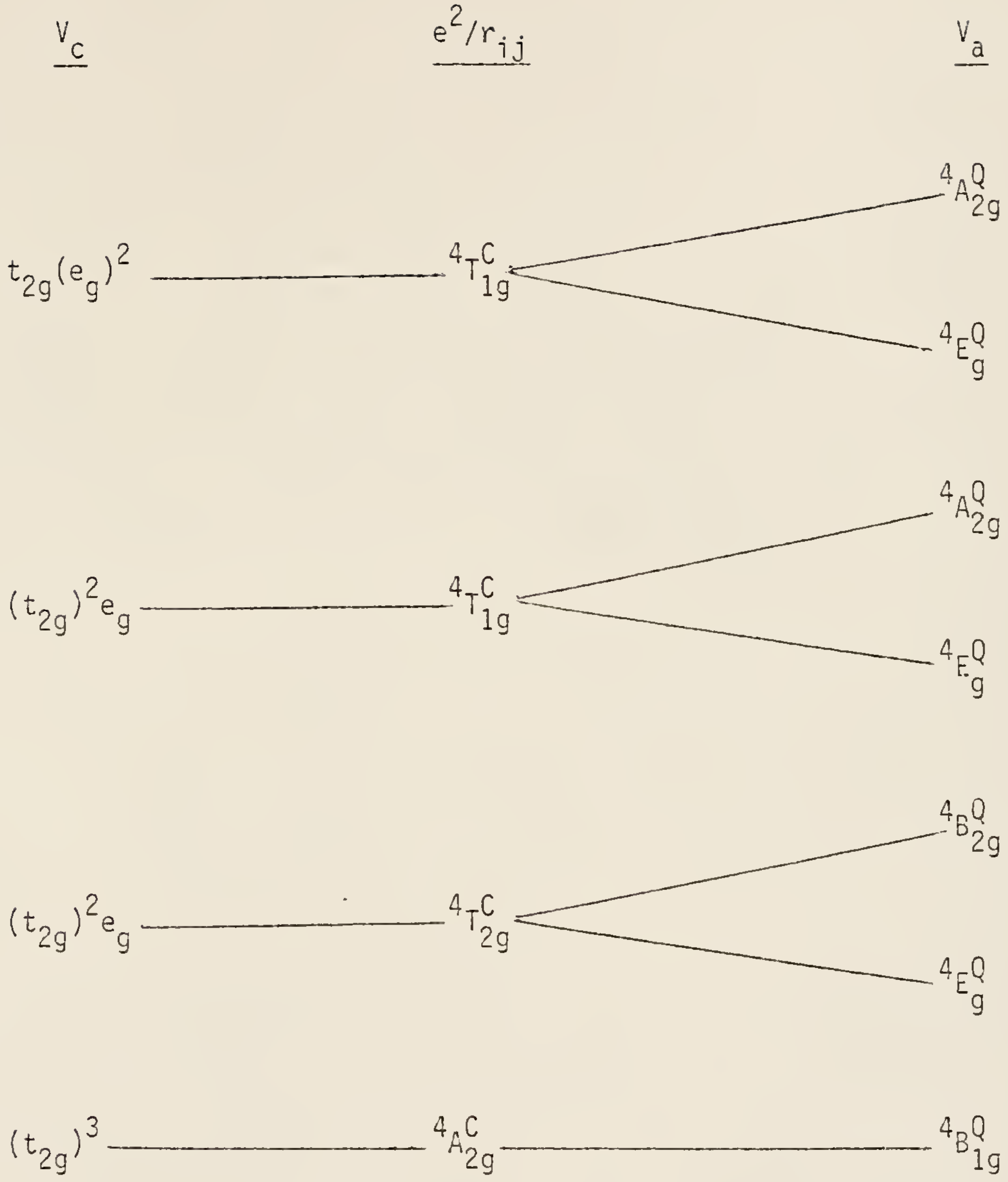

Figure 13. The Quartet Ground State and the Six Quartet Excited States Expected (Spin-Orbit Interaction Neglected) for a Tetragonal Chromium (III) Complex.

of these five lowest energy intraconfigurational doublets while simultaneously fitting the observed spin-allowed bands serves as a justification of the six parameter theory that we have used. Second, the interelectronic repulsion parameter C can be evaluated. Third, by fitting the spin-orbital levels of $^2E_g^Q$ (Γ_6^Q and Γ_7^Q) the spin-orbit parameter ζ can be evaluated.

For many tetragonal complexes the splitting of either or both of $^4T_{2g}^C$ and $^4T_{1g}^C$ is not great enough to allow resolution of the individual tetragonal components. This can make the exact evaluation, based on the spin-allowed transitions, of the parameters Dq, B, Dt and Ds impossible. Nonetheless, even if the tetragonal splitting is not resolved it may be possible to set reasonable upper limits for the magnitudes of Dt and/or Ds. That is, the values chosen for Dt and Ds should predict a relatively small tetragonal splitting when the tetragonal components are not resolved. It is reasonable to assume that splittings greater than 1500 cm^{-1} should be resolved. This criterion allows for the placing of reasonable upper limits to the magnitudes of the values of Dt and Ds when the tetragonal splitting of the spin-allowed bands is not observed. Also, the positions of the unsplit spin-allowed transitions allow for reasonable estimates to be made for Dq and B.

A survey of the literature has indicated that the ligand field theory does not predict very well the tetragonal splitting of $^2E_g^C$ when the tetragonal splitting of the spin-allowed bands is not observed.[1] In this case the theory generally predicts a splitting of less than 100 cm^{-1} whilst the experimentally observed splitting is generally 200 cm^{-1} or more.[2] On the other hand, when the tetragonal splitting of the spin-allowed bands is observed the theory has been found to reproduce the tetragonal splitting of $^2E_g^C$ fairly well.[3]

For the most part, the debate on the applicability of the theory to the spin-forbidden transitions has centered on this tetragonal splitting of $^2E_g^C$ into $\Gamma_6^Q(^2A_{1g}^Q)$ and $\Gamma_7^Q(^2B_{1g}^Q)$.[4] This limitation is probably due to the fact that the tetragonal components of $^2E_g^C$ are often the two lowest energy doublet states and, hence, the easiest to identify in the spectra of the various tetragonal systems.[5] The three tetragonal components of $^2T_{1g}^C$ are seldom all identified for a single complex. Therefore, we believe it is important to study those systems for which the electronic origins corresponding to all five lowest energy intraconfigurational doublet transitions have been identified.

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[1] C. D. Flint and A. P. Matthews, J.C.S. Faraday II, 69, 419(1973); and T. Schönerr and H.-H. Schmidtke, Inorg. Chem., 18, 2726(1979)

[2] Ibid.

[3] C.D. Flint and A. P. Matthews, J.C.S. Faraday II, 70, 1307 (1974); C. D. Flint and A. P. Matthews, Inorg. Chem., 14, 1008(1975).

[4] Ibid; T. Schönherr and H.-H. Schmidtke, Inorg. Chem., 18, 2725 (1979); C. D. Flint and A. P. Matthews, J.C.S. Faraday II, 69, 419 (1973); T. Schönherr and H.-H. Schmidtke, Z. Anorg. Allg. Chem., 443, 225(1978); and S. DeCurtins, H. U. Güdel and K. Neuenschwander, Inorg. Chem., 16, 796(1977).

[5] T. Schönherr and H.-H. Schmidtke, Inorg. Chem., 18, 2726(1979); T. Schönherr and H.-H. Schmidtke, Z. Anorg. Allg. Chem., 443, 225 (1978); C. D. Flint and A. P. Matthews, J.C.S. Faraday II, 69, 419 (1973); and S. DeCurtins, H. U. Güdel and K. Neuenschwander, Inorg. Chem., 16, 796(1977).

We have found in the literature two tetragonal chromium (III) complexes for which these five lowest energy spin-forbidden doublets have been identified.[1] The complex ions are trans-bis(pyridine-1,5-dicarboxylato)chromate (III) and isocyanato(pentaammine)chromium (III).[2] The site symmetry of trans-$[Cr(PDC)_2]^-$, which has the chromophore trans-CrN_2O_4, is D_{4h}. The site symmetry of $[Cr(NH_3)_5(NCO)]^{+2}$ is less than D_{4h} (being only C_{4v}). The tetragonal energy matrices can be applied to this complex, however, if we assume an average tetragonal field.

In Table 53 the ligand field and Racah parameters for trans-$[Cr(PDC)_2]^-$ and $[Cr(NH_3)_5(NCO)]^{+2}$ are given. These parameters have been evaluated by fitting the bands, both spin-forbidden and spin-allowed, which have been reported in the literature, using the tetragonal energy matrices that we have described herein.

In Table 54 the observed and the calculated positions of the five lowest energy intraconfigurational spin-forbidden transitions for trans-$[Cr(PDC)_2]^-$ and $[Cr(NH_3)_5(NCO)]^{+2}$ are given. In Table 55 the observed and the calculated positions for the four lowest energy spin-allowed transitions for the two complexes are given.

We will discuss the spectral fit and the resulting parameters for trans-$[Cr(PDC)_2]^-$ and $[Cr(NH_3)_5(NCO)]^{+2}$ individually below. Lastly,

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[1] T. Schönherr and H.-H. Schmidtke, Inorg. Chem., 18, 2726(1979); T. Schönherr and H.-H. Schmidtke, Z. Anorg. Allg. Chem., 443, 225 (1978); P. E. Hoggard and H.-H. Schmidtke, Chem. Phys. Letters, 20, 119(1973); and C. D. Flint and A. P. Matthews, J.C.S. Faraday II, 71, 379(1975).

[2] The following abreviation will be used: PDC = pyridine-2,6-dicarboxylato.

TABLE 53

The Ligand Field and Racah Parameters for Trans-$[Cr(PDC)_2]^-$
and $[Cr(NH_3)_5(NCO)]^{+2}$

All parameters listed below are in reciprocal centimeters (cm^{-1})

Complex	Dq	B	C	Dt	Ds	ζ
Trans-$[Cr(PDC)_2]^-$	1780	600	2784	100	-300	200
$[Cr(NH_3)_5(NCO)]^{+2}$	2100	700	3220	-160	240	265

TABLE 54

The Observed and the Calculated Band Positions
for the Spin-Forbidden Transitions in
Trans-$[Cr(PDC)_2]^-$ and
$[Cr(NH_3)_5(NCO)]^{+2}$

All band positions listed below are in
reciprocal centimeters (cm^{-1})

Observed	Calculated	Assignment
	a) Trans-$[Cr(PDC)_2]^-$	
12,735	12,835	$\Gamma_6^Q[^2A_1^Q(^2E^C)]$
12,910	12,889	$\Gamma_7^Q[^2B_1^Q(^2E^C)]$
13,060	13,058	$\Gamma_7^Q[^2E^Q(^2T_1^C)]$
13,162	13,177	$\Gamma_6^Q[^2E^Q(^2T_1^C)]$
13,285	13,364	$\Gamma_6^Q[^2A_2^Q(^2T_1^C)]$
	b) $[Cr(NH_3)_5(NCO)]^{+2}$	
14,678	14,860	$\Gamma_7^Q[^2B_1^Q(^2E^C)]$
14,891	14,905	$\Gamma_6^Q[^2A_1^Q(^2E^C)]$
15,256	15,233	$\Gamma_6^Q[^2E^Q(^2T_1^C)]$
15,378	15,307	$\Gamma_7^Q[^2E^Q(^2T_1^C)]$
15,424	15,518	$\Gamma_6^Q[^2A_2^Q(^2T_1^C)]$

TABLE 55

The Observed and the Calculated Band Positions for the Spin-Allowed Transitions in Trans-$[Cr(PDC)_2]^-$ and $[Cr(NH_3)_5(NCO)]^{+2}$

All band positions listed below are in reciprocal centimeters (cm^{-1})

a) Trans-$[Cr(PDC)_2]^-$

Observed	Calculated	Assignment
17,800	17,803	${}^4B_2^Q({}^4T_2^C)$
	18,663	${}^4E^Q({}^4T_2^C)$
26,500	23,502	${}^4A_2^Q({}^4T_1^C)$
28,100	25,242	${}^4E^Q({}^4T_1^C)$
	b) $[Cr(NH_3)_5(NCO)]^{+2}$	
20,300	19,683	${}^4E^Q({}^4T_2^C)$
	21,007	${}^4B_2^Q({}^4T_2^C)$
27,300	27,015	${}^4E^Q({}^4T_1^C)$
	28,236	${}^4A_2^Q({}^4T_1^C)$

we will compare and discuss the results for these two complexes, taken together, with those reported in the literature.

Trans-$[Cr(PDC)_2]^-$

The spin-allowed spectra (diffuse reflectance) for trans-$[Cr(PDC)_2]^-$ has been reported by Schmidtke and Hoggard.[1] Spin-forbidden spectra, of interest, has been reported by Flint and Matthews.[2]

The tetragonal splitting of the first cubic spin-allowed transition is not observed while that of the second cubic spin-allowed transition is resolved. No polarized work has been done for this complex. Therefore, the assignments of the spin-allowed components must be based on other considerations.

The parameter Dt, which determines the splitting of the first band, can be shown to be

$$Dt = (4/7)[Dq(z)-Dq(xy)]$$

where Dq(z) and Dq(xy) are the cubic ligand field parameters corresponding to the axial and the equatorial ligands, respectively. It is well-known that ligands which bond through nitrogen exert a greater ligand field than do ligands which bond through oxygen. Therefore, it is likely that Dt will be positive for this complex and that ${}^4B^Q_{2g}({}^4T^C_{2g})$ will be the lowest energy spin-allowed state.

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[1] P. E. Hoggard and H.-H. Schmidtke, Chem. Phys. Letters, 20, 119 (1973).

[2] C. D. Flint and A. P. Matthews, J.C.S. Faraday II, 71, 379(1975).

The value of Dq for trans-$[Cr(PDC)_2]^-$ can be approximated from the position of the first (unsplit) spin-allowed band. The values of the interelectronic repulsion parameters B and C, the axial ligand field parameters Dt and Ds, and the spin-orbit parameter ζ are determined by best fitting the five lowest energy spin-forbidden transitions and the three spin-allowed bands which have been observed. In particular, the values of C is determined by a near exact fit of the lowest energy tetragonal component arising out of ${}^2T_{1g}^C$. The fit of this particular spin-forbidden band gives the best overall fit for the five lowest energy intraconfigurational doublets. The values of these parameters are given in Table 53 and the results of the fitting are given in Tables 54a and 55a.

The assignments which result from our fitting (table 54a) for the spin-forbidden bands agree with the assignments, based primarily on intensity considerations and a vibrational analysis, made by Flint and Matthews.[1]

For trans-$[Cr(PDC)_2]^-$ we find that our fitting results in a splitting of 54 cm^{-1} for the tetragonal components of ${}^2E_g^C$ whilst the experimentally observed splitting is 175 cm^{-1}. For the energy separation between the higher energy tetragonal component of ${}^2E_g^C$ and the lowest energy tetragonal component of ${}^2T_{1g}^C$ our fitting is found to be 169 cm^{-1} whilst the experimentally observed separation is 150 cm^{-1}. Further, our fitting results in a splitting of 119 cm^{-1} for the spin-orbital levels of ${}^2E_g^Q({}^2T_{1g}^C)$ whilst the experimentally observed splitting is 102 cm^{-1}. This is an excellent agreement and has been obtained with a reasonable value of 200 cm^{-1} for the spin-orbit parameter.

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[1] Ibid.

In summary, for trans-$[(Cr(PDC)_2]^-$ we note that the fit of the five lowest energy spin-forbidden bands is, overall, very good. Three of these five spin-forbidden bands are reproduced by our fitting to within 20 cm^{-1} and the remaining two spin-forbidden bands are reproduced to within 100 cm^{-1}.

The tetragonal splitting of $^4T_{2g}^C$ is predicted to be 860 cm^{-1} for the parametric values we have chosen in order to fit the spin-forbidden bands as accurately as possible. This small value predicted for this splitting is consistent with the experimental fact that the tetragonal components of $^4T_{2g}^C$ are not resolved. The tetragonal splitting of $^4T_{1g}^C$ is predicted to be 1740 cm^{-1} whilst the experimentally observed splitting is 1600 cm^{-1}. However, the actual positions of the tetragonal components of $^4T_{1g}^C$ are predicted by our fitting to be about 3000 cm^{-1} lower than where they are actually observed.

The positions of the tetragonal components of $^4T_{1g}^C$ can be better reproduced using large B value (ca. 900 cm^{-1}). However, the spin-forbidden bands are very poorly reproduced with such a B value. Probably this system needs further study (such as polarized work) to obtain better resolution and definitive assignments of the spin-allowed bands.

$[Cr(NH_3)_5(NCO)]^{+2}$

The spin-allowed spectra (aqueous solution) for $[Cr(NH_3)_5(NCO)]^{+2}$ has been reported by Schmidtke and Schönherr.[1] The spin-forbidden spectra, of interest, has also been reported by these authors.[2] Schmidtke and Schönherr's efforts towards fitting centered on an attempt to reproduce the tetragonal splitting of $^2E_g^C$. The effort fails here, as elsewhere, to reproduce this particular splitting with a reasonable set of parameters. Apparently, because of this these authors did not attempt to examine how well the theory could reproduce the tetragonal components of $^2T_{1g}^C$.

The tetragonal splittings of the first and the second cubic spin-allowed transitions are not observed. The sign of Dt is taken to be negative since ammonia exerts a greater ligand field than does the isocyanato ion.[3]

The value of the cubic ligand field parameter Dq can be approximated from the position of the first (unsplit) spin-allowed band. The values of the interelectronic repulsion parameters B and C, the axial ligand field parameters Dt and Ds, and the spin-orbit interaction parameter ζ are determined by best fitting the five lowest energy spin-forbidden transitions and the two spin-allowed bands which have been observed. Just as for trans-$[Cr(PDC)_2]^-$ the value of the interelectronic repulsion parameter C is determined by a good fit of the lowest energy tetragonal component of $^2T_{1g}^C$. This is done to obtain the best possible fit of the five lowest energy intraconfigurational doublets. The values of these parameters are given in Table 53 and the results of the fitting given in Tables 54b and 55b.

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[1] T. Schönherr and H.-H. Schmidtke, Z. Anorg. Allg. Chem., 443, 225(1978).

[2] T. Schönherr and H.-H. Schmidtke, Inorg. Chem., 18, 2726(1979).

[3] T. Schönherr and H.-H. Schmidtke, Z. Anorg. Allg. Chem., 443, 225(1978).

The assignments which result from our fitting (Table 54b) for the spin-forbidden bands agree with the assignments, based primarily on intensity considerations and a vibrational analysis, made by Schmidtke and Schönherr.[1]

For this complex we find that our fitting results in a splitting of 45 cm^{-1} for the tetragonal components of $^2E_g^C$ whilst the experimentally observed splitting is 213 cm^{-1}. For the energy separation between the higher energy tetragonal component of $^2E_g^C$ and the lowest energy tetragonal component of $^2T_{1g}^C$ our fitting yields 328 cm^{-1} whilst the experimentally observed separation is 365 cm^{-1}. For the splitting of $^2E_g^Q(^2T_{1g}^C)$ into Γ_6^Q and Γ_7^Q by the spin-orbit interaction our fitting yields 74 cm^{-1} whilst the experimentally observed splitting is 122 cm^{-1}. This agreement has been obtained with a reasonable value of 265 cm^{-1} for the spin-orbit parameter.

In summary, for $[Cr(NH_3)_5(NCO)]^{+2}$ we note that the fit of the five lowest energy intraconfigurational spin-forbidden bands is, overall, good. Two of the five spin-forbidden bands are reproduced by our fitting to within 20 cm^{-1} and two of the remaining three doublets are reproduced to within 100 cm^{-1}. Only the lower energy tetragonal component of ${}^2E_g^C$ is not well-reproduced by our fitting.

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[1] T. Schönherr and H.-H. Schmidtke, Inorg. Chem., 18, 2726(1979).

The tetragonal splittings of ${}^4T_{2g}^C$ and ${}^4T_{1g}^C$ are predicted to be 1324 cm^{-1} and 1221 cm^{-1}, respectively, for the parametric values we have chosen. The small values predicted for these splittings are consistent with the experimental fact that the tetragonal components of ${}^4T_{2g}^C$ and ${}^4T_{1g}^C$ are not resolved. The actual positions of the unsplit spin-allowed bands agree well with the positions predicted by our fitting for the tetragonal components.

Summary and Discussion

In summary for trans-$[Cr(PDC)_2]^-$ and $[Cr(NH_3)_5(NCO)]^{+2}$, we find that: (1) the five spin-forbidden transitions predicted by the theory are observed; (2) the energy separation between the higher energy tetragonal component of ${}^2E_g^C$ and the lowest energy tetragonal component of ${}^2T_{1g}^C$ can be fitted very well; (3) the splitting of ${}^2E_g^O({}^2T_{1g}^C)$ into its spin-orbital levels can be fitted very well; (4) the positions of the five lowest energy intraconfigurational doublets are well-reproduced; and (5) the tetragonal splitting of ${}^2E_g^C$ is not well-reproduced.

The failure to reproduce the tetragonal splitting of ${}^2E_g^C$ is consistent with previous reports in the literature which indicate that when the tetragonal splitting of the spin-allowed bands is not observed, then the tetragonal splitting of ${}^2E_g^C$ will be significantly underestimated by the theory.[1] Güdel has postulated that the tetragonal splitting of $^2E_g^C$ is so small as not to be resolvable under normal conditions.[1] Güdel's explanation cannot be applied for trans-$[Cr(PDC)_2]^-$ and $[Cr(NH_3)_5(NCO)]^{+2}$ since all five lowest energy spin-forbidden bands have been identified, unless one of the electronic origins has been falsely identified. Flint has attributed the failure of the theory to reproduce the tetragonal splitting of $^2E_g^C$ to the fact that the spherical interelectronic repulsion parameter B is employed.[2] However, the necessity of B as an average parameter is forced upon us by the virtual impossibility of ever evaluating the individual components into which B can be broken. That is, when the d electron approximation is abandoned, a myriad of parameters arise for the interelectronic repulsions. Thus, instead of two spherical parameters, B and C, 10 cubic and 23 tetragonal interelectronic repulsion parameters arise in the more generalized ligand field theory. It is not possible to obtain values for so many parameters when the total number of observed transitions are so few.

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[1] C. D. Flint and A. P. Matthews, J.C.S. Faraday II, 69, 419(1973); and T. Schönherr and H.-H. Schmidtke, Inorg. Chem., 18, 2726(1979).

It is also worth noting that the values for the interelectronic repulsion parameters B and C and the spin-orbit parameter ζ are considerably smaller for trans-$[Cr(PDC)_2]^-$ than they are for $[Cr(NH_3)_5(NCO)]^{+2}$. This may indicate a greater degree of covalency in trans-$[Cr(PDC)_2]^-$.

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[1] S. DeCurtins, H. U. Güdel and K. Neuenschwander, Inorg. Chem., 16, 796(1977).

[2] C. D. Flint and A. P. Matthews, J.C.S. Faraday II, 69, 419 (1973).

Further application of our complete energy level calculations should await more thorough experimental studies of other tetragonal systems. These studies should not only uncover all the intraconfigurational doublets and the tetragonal split components of the spin-allowed bands, but should also result in definitive assignments of the bands.

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BIOGRAPHICAL SKETCH

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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